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Mosaic Crystals of Zinc

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Optically mosaic crystals of zinc have been grown by the Czochralski-Gomperz method. Three types have been distinguished. During growth mosaic crystals frequently change from one type to another. The conditions of growth under which they were obtained are described briefly. As yet their genesis and their evolutions during growth cannot be controlled or predetermined.

DURING experiments on the growth of single crystals of zinc by the Czochralski-Gomperz method the writer has obtained several hundred specimens with "optically mosaic" structure.[1] The term "mosaic" may properly be applied, as it is in the literature of nonmetallic crystal physics,[2] to a crystal having a "broken" cleavage surface which consists of plane areas each slightly differently oriented with respect to its neighbors. When these elementary areas are large enough to be observed with a low power microscope or the unaided eye, the crystal may be called optically mosaic.

The three distinct types of such mosaics encountered are illustrated by Figs. 1 to 3, which are photomicrographs of unetched, unpolished, natural cleavage surfaces.[3] In type A, Fig. 1, the components of the mosaic pattern have irregular boundaries and are small compared to the whole surface. An entire cleavage surface may consist of mosaic elements, as in the figure, or the mosaic pattern may be confined to only a part of it. The differences in orientation, shown in the photograph by the differences in brightness of neighboring areas, are usually less than a degree. That each area is itself plane is shown by the fact that any given one always appears equally bright all over. In type B, Fig. 2, there are large areas bounded usually by straight lines and occasionally by smooth curves. The angle of tilt between two neighboring areas may amount to 1 or 2 degrees. In type C, Fig. 3, the elementary mosaic areas are bounded by nearly parallel lines which to the unaided eye appear straight, but which under greater magnification are seen to be jagged. For crystals having orientations of 35° or more these bounding lines are always very nearly parallel to the major axis of the elliptical cleavage surfaces of the writer's circular cross section crystals.

A single mosaic type does not necessarily persist throughout a crystal of 8–10 cm length. Frequently the ends of a specimen may be of different types with a region of transition between, or the same type, neither mosaic or single, may occur at both ends, the middle being quite different. Changes from one type to another occur

[1] The writer has just learned that similar mosaic zinc crystals were grown by Dr. James E. Brock about three years ago in the Physical Laboratory at Purdue University. The method of growth, however, was not the Czochralski-Gomperz method but the one devised by Bridgman.

[2] Wien-Harms, Ott, Handb. d. Exp. Physik **7**, 2nd part, 101, 102.

[3] Basal planes of the zinc crystal.

FIG. 1. Type A mosaic crystal. Diameter of area photographed = $D = 3.3$ mm.

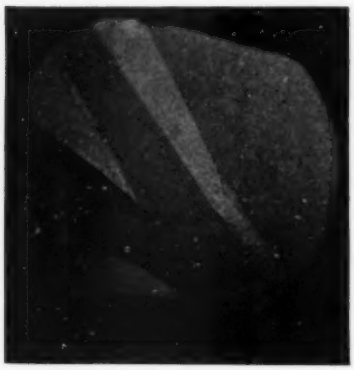

FIG. 2. Type B. $D = 6.4$ mm.

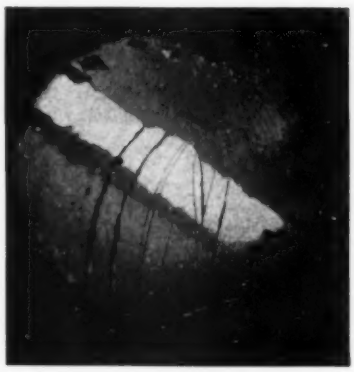

FIG. 3. Type C. $D = 4.4$ mm.

apparently at any speed, sometimes taking place during only a few mm of growth, and sometimes requiring 10 or 20 cm of growth for their completion. In the majority of cases the course of such changes is quite unpredictable. However, one typical evolution, a case of change from single to type C structure and back to single, has been observed. Its various stages, which are quite invariable in their sequence, are sketched in Figs. 4 and 5. The positions along the crystal of successive cleavages (for a crystal having an orientation of approximately 45°) and the appearances of corresponding surfaces are represented by a, b, c, etc., of the two figures. Section a (near the top or nucleus end of the crystal) is optically single. The next section, b, shows a small area of slightly different orientation making its appearance at the upper end of the major axis b′. In the following sections this area increases in size, growing first mainly along the major and axis, then becoming wider until there are three distinct parallel-edged areas. Two of these are then crowded out by degrees until finally we again have an apparently good surface (h) which may have the same orientation as (a) or one slightly different. While scores of such evolutions have been observed, not a single one has been found in which the invading area made its appearance at the lower end of the major axis (at b in Fig. 5). Nor does it ever make its appearance on the sides of the elliptical periphery, though it may grow down one side of the major axis turning the crystal into a double of type C, as illustrated by Fig. 6, a to e, instead of the triple as in the previous one.

The apparatus was essentially that of Hoyem[4] except that the crystals were grown in air. The growing procedure was at first as near as possible that of Hoyem and Tyndall,[5] though later modifications were made which need not be described here. Various speeds between 0.1 cm/min. and 8 cm/min. were used. Great care was taken to ensure uniform motion of the drawing apparatus and to prevent vibration. The specimens were from 8 to 30 cm in length and from 0.2 cm to 1.1 cm in diameter. The diameter could with care be kept uniform to within 0.01 cm. Mosaics have been grown over a temperature range extending 50° above the melting point of zinc and over the whole orientation range. During growth the temperature of the molten zinc in the crucible immediately below the growing crystal was maintained constant to within 0.5°C. The rate of discharge of the air blast directed from a ring nozzle to the crystal at a point 1.5 cm above the melt was constant.

Nine different brands or lots of zinc were used. With one exception they were all of reagent grade and some certainly contained not more than 0.001 percent of impurity. Mosaics were obtained from all these zincs although there were some slight differences in the type produced, etc., in the various lots.

Mosaics could appear when either a single or a mosaic nucleus was used to inoculate the growing crystal. In spite of the maintenance of very rigid control of all the factors ordinarily considered important in crystal growth, it has thus far been

[4] Hoyem, Phys. Rev. **38**, 1358 (1931).

[5] Hoyem and Tyndall, Phys. Rev. **33**, 81 (1929).

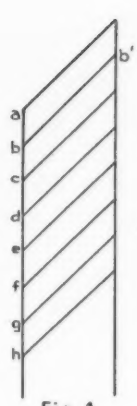

Fig. 4

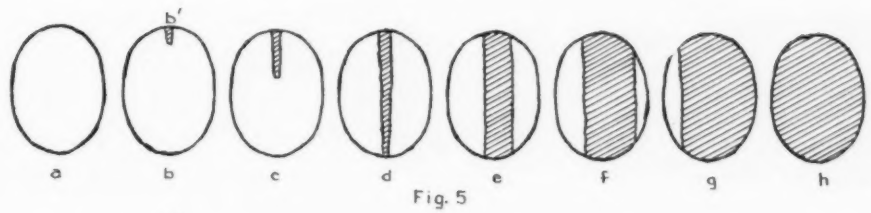

Fig. 5

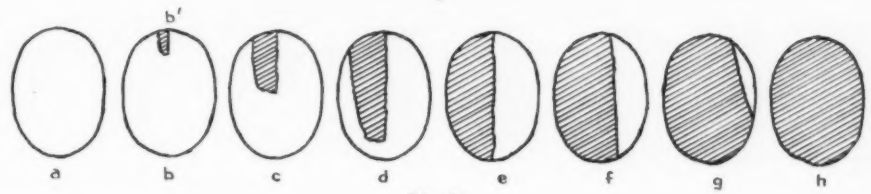

Fig. 6

FIGS. 4–6. Stages of typical evolutions from single to type C structure and back to single.

impossible to control the appearance of mosaics or prevent the occurrence of evolutions during growth. *Both mosaic and single crystals have been obtained* for most lots of zinc *under apparently identical conditions of growth.* The investigation is being continued in the hope of discovering why the writer's experience is so different from that of previous workers, in this laboratory and elsewhere, who grew single crystals with no difficulty and encountered no mosaics.

This work is being done under the direction of Professor E. P. T. Tyndall, to whom the writer is greatly indebted for many suggestions and for encouragement.

Diffusion Through a Membrane

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An exact solution is obtained for the problem of diffusion through a membrane separating two stirred solutions of different concentrations. For a diffusion cell in which the two liquid containers have the same volume and for which the ratio λ ("effective" volume of membrane : volume of liquid) is small compared with unity, the solution gives explicit expressions for the concentrations at any time in terms of the initial distribution of concentration in the membrane. Two cases are treated: (1) zero initial concentration in the membrane and in one of the liquids; (2) an initial linear concentration gradient connecting the concentrations in the two containers. The usual assumption of a linear gradient across the membrane during the whole course of diffusion will not lead to an appreciable error in a determination of a diffusion constant unless λ exceeds 0.1 or the time of diffusion is much shorter than in the usual practice. Since λ is about 0.02 in the usual type of diffusion cell the use of the simple expression based on a linear gradient cannot be in error. If, however, the preliminary treatment of the membrane fails to yield an initial linear gradient in it, an appreciable error will be made even with λ less than 0.02.

1. INTRODUCTION

A SIMPLE and precise method for the determination of diffusion constants involves the use of a diffusion cell in which a porous membrane separates two homogeneous liquids.[1] Thus a solution of concentration v_0 is placed on one side A of the membrane and pure solvent on the other side B. The membrane is given a preliminary treatment to justify some statement about the initial distribution of the solute in it. Diffusion is allowed to proceed for a definite time, the liquids being kept homogeneous by (say) stirring. The concentrations in A and B change from their original values v_0, 0 to different values v, w in the time t, and from a knowledge of these final values it is desired to find the diffusion constant of the solute.

It is usual to assume that the preliminary treatment of the membrane can be made to give an initial *linear* distribution across it and that linearity is maintained during diffusion.[2] If the two containers A, B have the same volume b and the membrane has an effective volume a (determined by the distribution and structure of the pores), the assumptions give at once the relations

$$v=\tfrac{1}{2}v_0(1+e^{-2\lambda k t/a^2}), \qquad w=\tfrac{1}{2}v_0(1-e^{-2\lambda k t/a^2}), \quad (1)$$

where k is the diffusion constant and $\lambda=a/b$; the amount of substance in the membrane remains constant. The cell-constant λ/a^2 is usually determined by calibrating the cell with a solute of known diffusion constant.

Whatever may be the opinion regarding the possibility of producing an *initial* linear gradient across the membrane, the assumption of a linear gradient during diffusion contradicts the exact equations for the problem. An exact solution from given initial conditions may, however, be found.[3]

2. GENERAL SOLUTION OF THE PROBLEM

Let the membrane be bounded by the planes $x=0$, $x=a$. Well-stirred solutions of initial concentrations v_0, w_0 are in contact with the two sides of the membrane; the first solution extends from $x=0$ to $x=-b$ and the second from $x=a$ to $x=a+c$. The initial distribution of concentration across

[1] J. H. Northrop and M. L. Anson, J. Gen. Physiol. **12**, 543 (1929).

[2] J. W. McBain and T. H. Liu, J. Am. Chem. Soc. **53**, 59 (1931).

[3] H. W. March and W. Weaver, Phys. Rev. **31**, 1072 (1928), have solved a related problem of the diffusion from a gel into a liquid.

the membrane is $u_0(x)$. After a time t the concentrations in the two solutions will be denoted by $v(t)$, $w(t)$ and the distribution in the membrane by $u(x, t)$.

The equation

$$\partial u/\partial t = k\partial^2 u/\partial x^2, \tag{2}$$

where k is the diffusion constant of the solute, is to be solved subject to the following initial and boundary conditions:

$$u(x, t)\to u_0(x), \qquad t\to 0, \qquad 0\leq x\leq a; \tag{3}$$

$$u(0, t)=v(t), \qquad u(a, t)=w(t), \qquad t>0; \qquad v(0)=v_0, \qquad w(0)=w_0; \tag{4}$$

$$\partial v/\partial t=(k/b)(\partial u/\partial x)_{x=0}, \qquad \partial w/\partial t=-(k/c)(\partial u/\partial x)_{x=a}, \qquad t>0, \tag{5}$$

the Eqs. (5) expressing the proportionality of rate of increase of concentration of solution to rate of supply of solute from the membrane.

The solution of (2) which vanishes at $x=0$ and at $x=a$ and which satisfies (3) is

$$u' = \sum_1^\infty{}_n\, C_n e^{-\alpha_n t} \sin\,(n\pi x/a), \tag{6}$$

where

$$C_n = (2/a)\int_0^a u_0(y) \sin\,(n\pi y/a)dy \tag{7}$$

and

$$\alpha_n = kn^2\pi^2/a^2. \tag{8}$$

The solution of (2) which corresponds to zero initial concentration in the membrane and the faces maintained, respectively, in contact with solutions of concentrations $v(t)$, $w(t)$ is known to be[4]

$$u'' = \int_0^t \{v(\tau)(\partial/\partial t)F_1(x, t-\tau)+w(\tau)(\partial/\partial t)F_2(x, t-\tau)\}d\tau, \tag{9}$$

where

$$F_1(x, t) = 1-x/a-(2/\pi)\sum_1^\infty{}_n(1/n)e^{-\alpha_n t}\sin\,(n\pi x/a) \tag{10}$$

and

$$F_2(x, t) = x/a+(2/\pi)\sum_1^\infty{}_n((-1)^n/n)e^{-\alpha_n t}\sin\,(n\pi x/a). \tag{11}$$

We may write

$$\begin{aligned} u'' &= -\int_0^t \{v(\tau)(\partial/\partial\tau)F_1(x, t-\tau)+w(\tau)(\partial/\partial\tau)F_2(x, t-\tau)\}d\tau \\ &= v_0F_1(x, t)+w_0F_2(x, t)+\int_0^t \{v'(\tau)F_1(x, t-\tau)+w'(\tau)F_2(x, t-\tau)\}d\tau, \end{aligned} \tag{12}$$

and the solution of (2) which satisfies (3) and (4) is simply $u=u'+u''$. The value of u so found from (6) and (12) gives

$$-a(\partial u/\partial x) = v-w+2\sum D_n e^{-\alpha_n t}\cos\,(n\pi x/a)+2\sum \cos\,(n\pi x/a)\int e^{-\alpha_n(t-\tau)}(v'-(-1)^n w')d\tau,$$

where

$$D_n = v_0-(-1)^n w_0-n\pi C_n/2. \tag{13}$$

Eqs. (5) now give, respectively,

[4] See, e.g., Carslaw, *Mathematical Theory of Heat Conduction in Solids*, 1921, pp. 18, 68.

$$-(ab/k)(\partial v/\partial t)=v-w+2\sum D_n e^{-\alpha_n t}+2\sum\int e^{-\alpha_n(t-\tau)}(v'-(-1)^n w')d\tau$$

and

$$+(ac/k)(\partial w/\partial t)=v-w+2\sum(-1)^n D_n e^{-\alpha_n t}+2\sum\int(-1)^n e^{-\alpha_n(t-\tau)}(v'-(-1)^n w')d\tau.$$

These equations will be satisfied identically by putting[5]

$$\partial v/\partial t=\sum_i A_i e^{-\xi_i t},\qquad \partial w/\partial t=\sum_i B_i e^{-\xi_i t}, \tag{14}$$

if the A_i, B_i, ξ_i satisfy the equations

$$A_i(ab/k-1/\xi_i+2\textstyle\sum_n 1/(\alpha_n-\xi_i))=B_i(-1/\xi_i+2\sum_n(-1)^n/(\alpha_n-\xi_i)), \tag{15}$$

$$B_i(ac/k-1/\xi_i+2\textstyle\sum_n 1/(\alpha_n-\xi_i))=A_i(-1/\xi_i+2\sum_n(-1)^n/(\alpha_n-\xi_i)), \tag{16}$$

$$D_n=\textstyle\sum_i(A_i-(-1)^n B_i)/(\alpha_n-\xi_i). \tag{17}$$

Eqs. (14) will provide the solution of the problem if (15), (16), (17) lead to unique values for the numbers A_i, B_i, ξ_i. With

$$z_i^2=\xi_i a^2/k, \tag{18}$$

the last three equations become

$$A_i(1/\lambda_1-\cot z_i/z_i)=-B_i(1/z_i\sin z_i), \tag{15'}$$

$$B_i(1/\lambda_2-\cot z_i/z_i)=-A_i(1/z_i\sin z_i), \tag{16'}$$

$$D_n'=kD_n/a^2=\textstyle\sum_i(A_i-(-1)^n B_i)/(n^2\pi^2-z_i^2), \tag{17'}$$

with

$$\lambda_1=a/b,\qquad \lambda_2=a/c. \tag{19}$$

Eliminating A_i, B_i from (15'), (16') we get the equation

$$z^2-(\lambda_1+\lambda_2)z\cot z-\lambda_1\lambda_2=0, \tag{20}$$

the real positive roots of which give the numbers ξ_i.

From (15') or (16') B_i is given in terms of A_i, ξ_i, and the infinite set of linear equations (17') provide the numbers A_i. Regarding the A_i, B_i, ξ_i as known, the concentrations of the two solutions are

$$v=\bar{u}-\textstyle\sum(A_i/\xi_i)e^{-\xi_i t},\qquad w=\bar{u}-\sum(B_i/\xi_i)e^{-\xi_i t}, \tag{21}$$

where $\bar{u}$, the final uniform concentration, is given by

$$\bar{u}(b+a+c)=v_0 b+\int_0^a u_0(x)dx+w_0 c. \tag{22}$$

From (21),

$$\textstyle\sum A_i/\xi_i=\bar{u}-v_0,\qquad \sum B_i/\xi_i=\bar{u}-w_0; \tag{23}$$

one of these is needed for the numerical evaluation of the A_i, B_i.

By means of (21) for v, w, the concentration distribution in the membrane is found from (6), (12) to be

$$u(x,t)=v(1-x/a)+wx/a-(2/\pi)\textstyle\sum_n(1/n)\sin(n\pi x/a)\sum_i(A_i-(-1)^n B_i)e^{-\xi_i t}/(\alpha_n-\xi_i). \tag{24}$$

It may be verified that this expression satisfies (2)–(5) when due account is taken of (21) and the conditions involved in (15')–(17'). The arguments necessary to make the above proof rigorous are elementary and readily supplied; they are omitted as providing nothing of interest.

[5] March and Weaver, reference 3; E. T. Whittaker, Proc. Roy. Soc. (London) **A94**, 367 (1917).

3. Application to Diffusion Experiments

In a usual type of apparatus constructed for measuring k the quantities $\lambda_1 = a/b$ and $\lambda_2 = a/c$ are equal and small compared with unity (of the order of $1/50$). The general solution may be adapted at once to this case and all the accuracy desirable in practical cases is obtained by disregarding powers of $\lambda (= \lambda_1 = \lambda_2)$ greater than the second, as negligible compared with unity. An equality sign will frequently be used where such an approximation has been made.

Let the positive roots of (20) with $\lambda_1 = \lambda_2 = \lambda$ be z_i, $i = 0, 1, \cdots$, arranged in order of magnitude; standard processes[6] for finding the roots of such an equation give

$$z_0 = (2\lambda)^{\frac{1}{2}}(1 - (1/12)\lambda + (11/1440)\lambda^2 - \cdots), \tag{25}$$

$$z_i = i\pi + 2\lambda/i\pi - 4\lambda^2/i^3\pi^3 + \cdots, \qquad i = 1, 2, \cdots. \tag{26}$$

When $\lambda_1 = \lambda_2$, (15′), (16′) show that

$$A_i = (-1)^{i+1} B_i$$

and the linear equations for the A_i become

$$D_n' = \sum_i A_i (1 + (-1)^{n+i})/(n^2\pi^2 - z_i^2). \tag{27}$$

The values of the A_i depend on the initial concentration in the membrane, i.e., on $u_0(x)$ of (3).

Case 1

A case of practical interest is that in which $u_0(x) = 0$, $w_0 = 0$; $D_n' = kv_0/a^2$. Here the Eqs. (27) become

$$E_n = \sum_1^\infty{}_i \, \alpha_{ni} A_i$$

with

$$E_n = kv_0/a^2 - [(1 + (-1)^n)/(n^2\pi^2 - z_0^2)]A_0, \qquad \alpha_{ni} = (1 + (-1)^{n+i})/(n^2\pi^2 - z_i^2).$$

The solution is[7]

$$A_i = (4\lambda/i^2\pi^2)A_0 - 2\lambda(kv_0/a^2)(1 - 4\lambda/i^2\pi^2), \qquad \text{for } i \text{ even},$$
$$A_i = -2\lambda(kv_0/a^2)(1 - 2\lambda/i^2\pi^2), \qquad \text{for } i \text{ odd}.$$

With the roots (26) these values of the A_i give

$$\sum_1^\infty A_i/z_i^2 = (\lambda/360)A_0 - \lambda(kv_0/a^2)(1/3 - 49\lambda/360),$$

and from the first of Eqs. (23), (25) and $\bar{u} - v_0 = -(v_0/2)(1 + \lambda/2 - \lambda^2/4)$, we get

$$(A_0/2\lambda)(1 + \lambda/6 + \lambda^2/90) + (kv_0/2a^2)(1 - \lambda/6 + \lambda^2/45) = 0.$$

Hence

$$A_0/\xi_0 = -(v_0/2)(1 - \lambda/6 + \lambda^2/60),$$
$$A_i/\xi_i = -(v_0/2)(4\lambda/i^2\pi^2)(1 - 6\lambda/i^2\pi^2) \qquad i \text{ even or odd}.$$

Thus

$$v = \frac{v_0}{2}\left(1 - \frac{\lambda}{2} + \frac{\lambda^2}{4} + \left(1 - \frac{\lambda}{6} + \frac{\lambda^2}{60}\right)e^{-2\lambda kt(1 - \lambda/6 + \lambda^2/45)/a^2} + \sum_1^\infty{}_i \frac{4\lambda}{i^2\pi^2}\left(1 - \frac{6\lambda}{i^2\pi^2}\right)e^{-kt(i^2\pi^2 + 4\lambda)/a^2}\right),$$

$$w = \frac{v_0}{2}\left(1 - \frac{\lambda}{2} + \frac{\lambda^2}{4} - \left(1 - \frac{\lambda}{6} + \frac{\lambda^2}{60}\right)e^{-2\lambda kt(1 - \lambda/6 + \lambda^2/45)/a^2} - \sum_1^\infty{}_i (-1)^i \frac{4\lambda}{i^2\pi^2}\left(1 - \frac{6\lambda}{i^2\pi^2}\right)e^{-kt(i^2\pi^2 + 4\lambda)/a^2}\right).$$

[6] See, e.g., Geiger-Scheel, Handb. d. Physik **3**, 600 (1928).

[7] Only two terms in the solution-series are needed: $\alpha_{ii}A_i = E_i - \sum_{k \neq i}{}_k \alpha_{ik} C_k/\alpha_{kk}$. For existence theorems see H. v. Koch, Jahresb. d. d. Math.-Verein. **22**, 289 (1913).

Case 2

Another case of interest is given by $u_0(x)=v_0(1-x/a)$, $w_0=0$; $C_n(\text{Eq. (6)})=2v_0/n\pi$, $D_n'=0$. Here the concentration gradient in the membrane is initially linear. In the notation of Case 1,

$$E_n=[(1+(-1)^n)/(n^2\pi^2-z_0^2)]A_0$$

and the α_{ni} are as before. The solution for the A_i is[8]

$$A_i=(4\lambda/i^2\pi^2)A_0 \qquad \text{for } i \text{ even},$$
$$A_i=0, \qquad \text{for } i \text{ odd}.$$

With these values the first of (23) gives, with $\bar{u}=v_0/2$,

$$kv_0/2a^2+(A_0/2\lambda)(1+\lambda/6+\lambda^2/90)=0.$$

Hence

$$A_0/\xi_0=-(v_0/2)(1-\lambda^2/180); \quad A_1/\xi_1=A_3/\xi_3=\cdots=0; \quad A_{2i}/\xi_{2i}=-(v_0/2)\cdot(\lambda^2/2\pi^4)\cdot(1/(2i)^4).$$

The concentrations v, w are thus

$$v=\frac{v_0}{2}\left(1+\left(1-\frac{\lambda^2}{180}\right)e^{-2\lambda kt(1-\lambda/6+\lambda^2/45)/a^2}+\frac{\lambda^2}{2\pi^4}\sum_1^\infty{}_i\,\frac{1}{i^4}e^{-4i^2\pi^2kt/a^2}\right),$$

$$w=\frac{v_0}{2}\left(1-\left(1-\frac{\lambda^2}{180}\right)e^{-2\lambda kt(1-\lambda/6+\lambda^2/45)/a^2}-\frac{\lambda^2}{2\pi^4}\sum_1^\infty{}_i\,\frac{1}{i^4}e^{-4i^2\pi^2kt/a^2}\right).$$

These equations indicate the error involved in the use of (1). The change from the exponent λ/a^2 in (1) to the exponent $\lambda(1-\lambda/6+\lambda^2/45)/a^2$ is of no experimental significance; either quantity represents a cell-constant determined by calibration. The error in (1) enters through the neglect of $\lambda^2/180$ in comparison with unity and the neglect of the terms following the first exponential. In the usual diffusion cell λ is of the order of 0.02 and $2\lambda kt/a^2$ is of the order 1 (diffusion proceeds until v is about $\frac{2}{3}v_0$). The terms following the first exponential are entirely negligible and the error introduced by the term $\lambda^2/180$ corresponds to an error of less than 1 in 10^6 in the concentration change. The deviations from (1) do not become appreciable until λ exceeds 0.1 and the time of diffusion is taken so short that the remaining terms of the series must be taken into account. Hence with the diffusion cell as ordinarily used no appreciable error will be introduced by the use of the simple expressions (1). A much greater error is to be expected if the initial gradient is not linear (Case 1).

I wish to thank Professor A. R. Gordon of the Department of Chemistry, University of Toronto, for suggesting the utility of an investigation of this problem.

[8] See footnote 7; only one term in the solution-series is now needed.

A Thermoelectric Metal-Crystal Analyzer

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A device is described which allows the measurement of the thermoelectric e.m.f. at room temperature for each increment of length of a metal test bar. A photographic arrangement permits a complete thermoelectric record of such a bar to be produced.

INTRODUCTION

IT is a well-known fact that the thermoelectric e.m.f. is a very sensitive function of the physical state of the sample upon which it is measured. Mechanical work within the elastic limits done by applying pressure or tension is known appreciably to change this property, as does work which exceeds the elastic limit. Heat treatment of material also produces measurable effects, as does magnetization of samples. Really large changes in e.m.f. from that exhibited by a pure metal may be produced by small alloying constituents and so on. With these facts in mind a form of apparatus which allows the measurement of the thermoelectric e.m.f. for each increment of length of a metal test bar was devised, with the expectation that such an arrangement would have many useful applications where physical changes as a function of position along such a bar are to be investigated. The first type of apparatus to accomplish this purpose was completed a number of years ago and has been described in detail elsewhere.[1] The present apparatus is an outgrowth of that one, though in no sense merely a refined version as there are differences in principle as well as detail involved.

Many obvious uses for an apparatus of this kind immediately suggest themselves. For instance, it could be used to check the uniformity of polycrystalline and single crystalline bars and thus serve as a production control. A study of residual effects resulting from various stress-strain conditions applied to a test bar could be made both in the elastic and plastic deformation regions. Experiments concerning heat-treatment and recrystallization effects as a function of some parameter, such as annealing temperature along the test bar, could be readily carried out. Thermoelectric effects produced by magnetization of various portions of a metallic bar could be investigated. In the study of metallic alloys this type of analysis is particularly fruitful as the function connecting thermoelectric e.m.f. with alloy-constituent concentration parallels the physical-structive, concentration function. The separation of alloying components upon crystallization also may be studied to advantage by this method and made to yield much information concerning crystal mechanics.[2]

THE PRINCIPLE OF THE THERMOELECTRIC ANALYZER

If a metal bar, placed in a recess possessing two regions of constant but different temperature, connected by a region having a steep heat gradient, Fig. 1, has its thermoelectric e.m.f. meas-

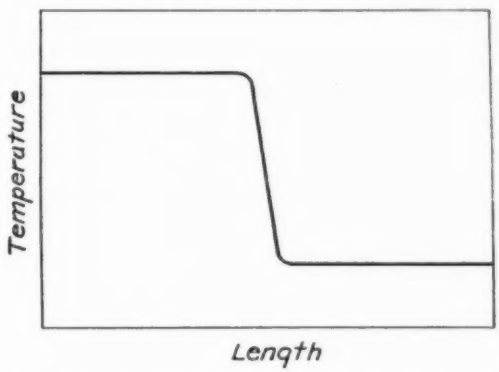

FIG. 1. Temperature distribution within the thermoelectric analyzer.

[1] A. Goetz and M. F. Hasler, Phys. Rev. **36**, 1752 (1930).

[2] Much literature exists on these various points; see any handbook of physics for a resumé.

ured by means of wires fastened to its ends, a value will be obtained which corresponds to the e.m.f. of that portion of the bar which subtends the temperature gradient. If the bar is moved through this gradient at such a rate that approximate thermal equilibrium is maintained, then the thermoelectric e.m.f. as a function of position along the bar may be recorded for its entire length. This constitutes the so-called *method of thermoelectric metal-crystal analysis.*

Method of Producing the Temperature Distribution

Since in this thermoelectric analyzer one is interested in changes along the length of a metal bar as well as the overall thermoelectric e.m.f. of bar to copper, say, which is usually measured, a very high degree of constancy is required, both in the temperature along the regions of constant temperature (Fig. 1) and in the difference of temperature between these regions. The magnitude of thermal fluctuation allowed was one-tenth of a percent of the temperature difference used. The method which achieves this result is essentially a self-regulating one in that differences of temperature which occur for any reason occur simultaneously in the two regions of different temperature and at a relatively slow rate, so that along the length of each, constancy of temperature is maintained as well as a constant difference between the two. Further, in order to maintain a steep temperature gradient between the two regions a large heat source and sink must be maintained. All these various requirements are met by using the method of water flows. Two identical systems thermally and electrically insulated were devised, Fig. 2, *A* and *B*, and are fed from a common source of water. The rate of flow through each is identical and since their heat capacities are likewise identical, the two systems fluctuate in unison with the temperature of the common water source. This remains the case when one of the flows is heated at a constant rate. Since the flows enter the apparatus at different temperatures, the cold one at the bottom of *A*, the hot one at the top of *B*, at adjoining points, a steep temperature gradient is maintained across this region and, since further heating or cooling does not occur, the remainder of the regions traversed by the flows are kept at constant temperatures. Constant pressure is maintained in the water systems by having the water fall through a constant height between inlets and outlets, while constant heating is effected by an electrical heater operated with large capacity storage batteries.

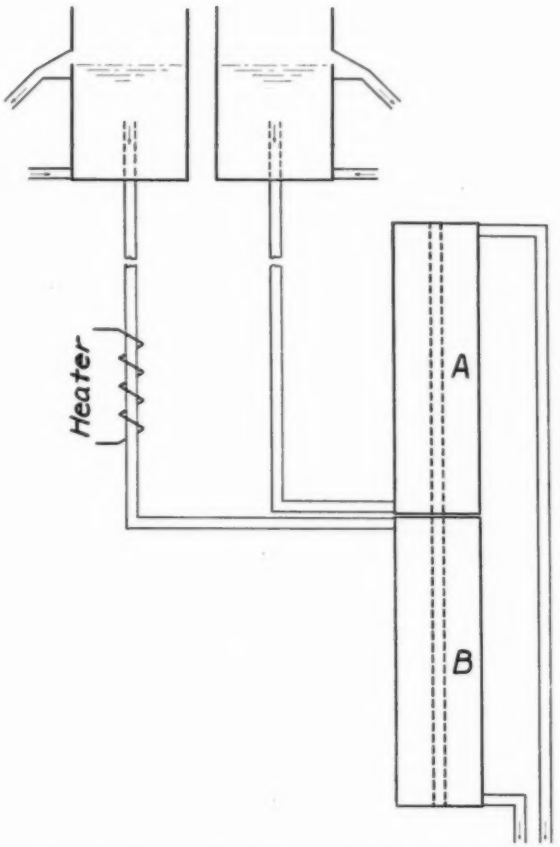

Fig. 2. Schematic diagram to illustrate the principle of the thermoelectric analyzer. The water streams keep *A* and *B* at different temperatures producing the temperature distribution along *A* and *B*, depicted in Fig. 1.

The Thermoelectric Analyzer Proper

In Fig. 2 chambers *A* and *B* are depicted with a continuous slot running their full lengths. It is in this slot that the metal bar to be analyzed moves. The chambers have a cross section as illustrated in Fig. 3, which also shows the position of the crystal at the center. Since the bar can only make contact with two walls its thickness is the only critical dimension, as upon it alone depends the thermal contact with these walls. In another

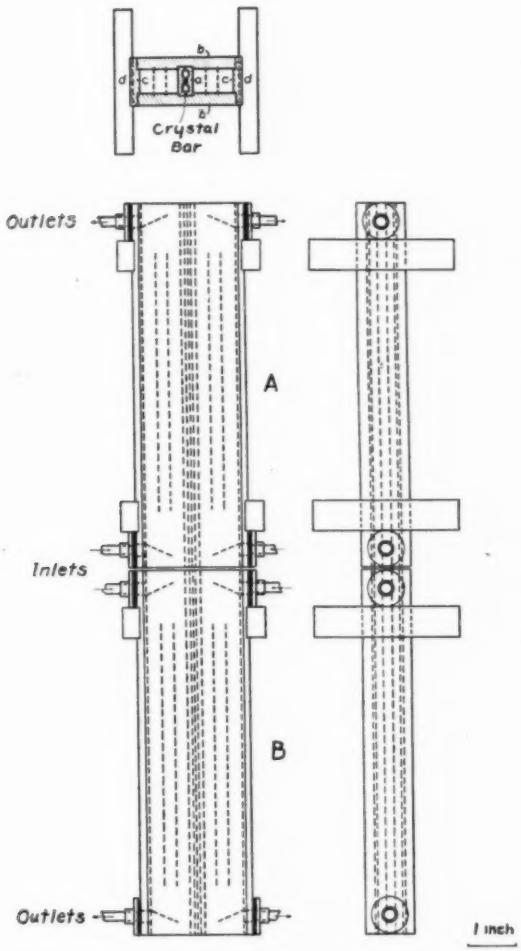

FIG. 3. A detailed drawing of the chambers *A* and *B* through which the crystal to be analyzed is moved.

paper[3] a method of growing single crystals possessing very exact dimensions was described, as was also a means of casting polycrystalline bars having this quality. Such test bars are suitable for investigation with this type of apparatus.

The constructional details of the chambers are also shown in Fig. 3. The materials used are copper and brass, the former being employed at all places where the heat conductivity must be a maximum, the latter at all other places. Thus the cavity in which the crystal moves has walls made of rectangular copper pieces *a*, shaped as indicated. The slot width which determines one crystal dimension is 0.0530″ and is accurate to 0.005″ along the whole length. Heavy brass side pieces *b*, slotted to allow the copper pieces to be wedged in tightly, hold the assembly rigid and supply necessary heat capacity to the system. Brass sides *c* and end plates of 0.010″ copper sheet complete the chamber walls. The various pieces are soldered together with water tight joints.

From Fig. 2 it is apparent that the temperature gradient must be maintained in the crystal by applying heat to it at the top of the bottom chamber and withdrawing it at the bottom of the top chamber. Thus at these points the water flows must be most effective. To do this copper-sheet baffles direct the incoming water against these points. In the body of the chamber, to facilitate the maintainence of a constant temperature, other copper pieces placed parallel to the flow have projections which introduce a stirring action. At the outlets similar arrangements are used as at the inlets, primarily to make the chambers symmetrical.

The two chambers are fastened together with the aid of cross bars *d*, which are bridged by wooden blocks. Metal tie rods hold these various blocks together. In a similar manner the two chambers are "hung up," so to say, by a similar set of blocks mounted toward the top of chamber *A* and supported by the main frame of the apparatus. Wood is used in this manner of supporting to provide thermal and electrical insulation between the two chambers. At the point where the chambers press together, a blotting paper washer 0.020″ in thickness, slotted to allow the passage of the crystal, furnishes insulation.

THE WATER SYSTEMS

The water systems, besides those portions made up of the chambers *A* and *B*, consist of inlet tanks and tubes, flow pipes and discharge tubes. The inlet tanks as shown in the schematic diagram (Fig. 2) have three openings each; an inlet at the bottom, an outlet a few inches above the bottom and an overflow near the top which provides a constant "head" for the system. Since these tanks are fed from the same water main and it is desirable to have the two chambers *A* and *B* electrically insulated, the inlet tubes consist of two eight feet 1/4″ rubber hoses. These furnish several hundred thousand ohms resist-

[3] M. F. Hasler, Rev. Sci. Inst. **4**, 656 (1933).

ance between the inlet tanks. These tanks, which are mounted directly under the ceiling, are connected to the analyzer chambers A and B by 1/4″ inside diameter copper tubings which branch at a point directly behind the analyzer to make a left and right connection to the corresponding halves of the chambers. The copper outlet pipes branch in a similar manner and discharge into a sink through glass tubes six feet in length which insulate the chambers A and B electrically. Adjustable jets on the ends of these tubes allow the water flows through the two systems to be made equal. This is an important condition since if it is not fulfilled changes in temperature which occur in the water source will not effect the two systems, which are of equal heat capacity, at the same rate.

The water which enters chamber B must be heated to provide the temperature gradient between A and B. This is accomplished by an electric heater made by winding three sections of No. 22 silk covered Advance wire on a four-foot glass tubing, which is made part of the connecting line from the inlet tank to the analyzer chamber. The three sections connected in parallel have a resistance of 24Ω.

The Recording System

To enable a continuous record to be made of the thermoelectric e.m.f. as a function of position along the crystal bar a photographic recording device is used. This is driven by a system of gears, worms and a rack, as illustrated in Fig. 4. The mechanical ratio is such that one revolution of the motor moves the plate 0.00096 in. Since it is essential that a fixed relationship be maintained between the crystal bar to be analyzed and the photographic plate, the bar is also moved by the same motor. To obtain various photographic resolving powers the crystal may be moved at the rates 1, 1/2, 1/4, 1/8 the speed of the photographic plate. This is accomplished by a sector of a circle which is driven by the same worm which moves the plate. The crystal bar may be connected by means of a steel tape to various radii of the sector, which move at the rates mentioned above. To enable changing from one speed to another, the analyzer chambers together with their entire water systems can be moved along

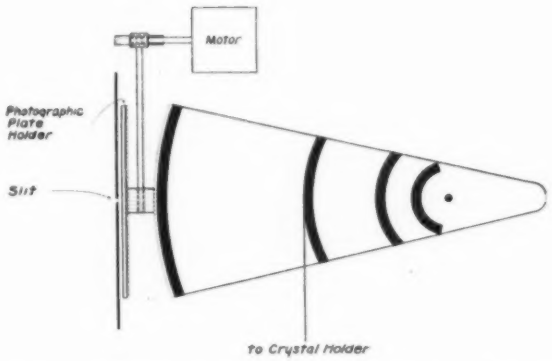

Fig. 4. Diagram of the recording device by which the photographic plate is moved in synchronism with the crystal. Ratios of plate to crystal speed obtainable are 1 : 1; 2 : 1; 4 : 1; 8 : 1.

on supporting rails so that the slot of the analyzer in which the crystal moves is directly below a driving radius.

The actual photographic record consists of the deflections of two galvanometers which are registered by light beams focussing images of vertical slits onto the stationary horizontal slit shown before the plate in Fig. 4.

The Crystal Bar Mounting

The crystal is supported and electrical connections made to it by means of a crystal holder. This is made of a wooden strip just thick enough to slide in the analyzer slot. A piece the size of the crystal to be used is cut out. Fine glass tubes, glued near the edges of the strip, contain the connecting wires which pass through the wood to the ends of the opening. When the holder is in the analyzer these tubes move in the wider slots at the side of the crystal-containing slot as shown in Fig. 3. Electrical contacts which also hold the crystal bar in place are made by soldering the connecting wires to the crystal in little recesses at the ends of the holder opening. For low melting point crystals, Wood's metal works quite well as a solder. A bent chromel wire electrically heated makes a suitable soldering iron for these small openings.

Besides the crystal this holder also carries a copper-constantan differential thermocouple to measure the temperature difference between the two chambers A and B. This is mounted in a separate glass tube which runs the length of the

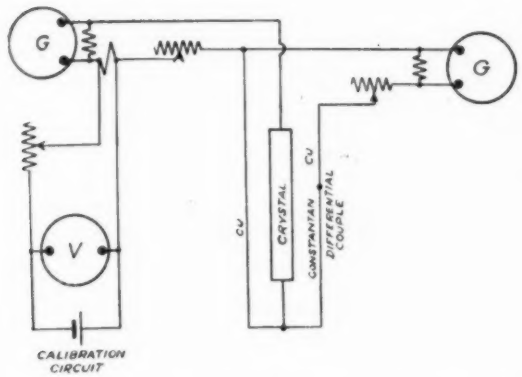

FIG. 5. Wiring diagram showing connections to the crystal and the differential thermocouple as well as those to the various recording and calibrating instruments.

holder. The constantan portion extends from a point adjacent to the center of the crystal bar to the lower end of the holder, where it connects with the lower crystal contact wire. These various connections are made clear in Fig. 5.

THE ELECTRICAL SYSTEM

Two galvanometers are used, one to measure the crystal bar's thermoelectric e.m.f., the other to measure the differential thermocouple's e.m.f. and hence ΔT. Since in general the changes in e.m.f. along the crystal bar will be small in comparison to the overall crystal to copper e.m.f., the latter is compensated with a bucking circuit so that high galvanometer sensitivities may be used in recording the former. This same circuit, Fig. 5, is used to calibrate the galvanometers after each run. This calibration is recorded directly on the same photographic plate so that all the necessary information for calculating absolute values of the thermoelectric power $\Delta E/\Delta T$ for any point on the crystal is contained in a permanent record.

The bucking circuit consists of a storage cell, a high precision voltmeter, a 1–100,000 ohm resistance box, and a 1-ohm standard resistance.

The highest sensitivity obtainable with the crystal e.m.f. measuring galvanometer adjusted for critical damping was 4.4 microvolts per cm at the plate while that used on the other galvanometer was 24 microvolts per cm. The distance from the plate to the galvanometers used was about 1 meter.

RESOLUTION OF THE ANALYZER

The resolution which is obtainable with the thermoanalyzer depends upon the temperature gradient which can be maintained between chamber A and B. This, in turn, depends upon the heat conductivity of the bar being analyzed and the amount of hot and cold water which can be run through the chambers per unit time. The first factor, for a bar of given material, depends only on the thickness of the bar, the analyzer slot being built accordingly. The second factor, for a given flow resistance determined by the dimensions of the apparatus, depends upon the non-fluctuating pressure head and power supply available.

Values for these various factors as used in the analyzer depicted herein may be of interest. The metal bars investigated were bismuth single crystals rectangular in shape with the critical thickness 0.051″. This size fits easily into the 0.053″ slot of the analyzer, the unoccupied thickness being filled with light lubricating oil to give thermal contact. Bismuth has a low heat conductivity so that a steep temperature gradient could be maintained along the crystal without excessive flows and the correspondingly high heating currents necessary to raise the temperature of the hot water a few degrees. With 600 watts on the heater a temperature difference of 4.75°C exists between the two chambers for a flow of 1840 cc per second. This whole temperature drop occurs over a 2 mm section of the crystal. Thus the thermoelectric e.m.f. for every 2 mm piece of crystal length is entirely resolved so to speak. Thermoelectric inhomogeneities of much less length than this can be partially resolved providing they represent large changes in the e.m.f. over that of the surrounding regions.

A SPECIFIC EXAMPLE

A typical record produced by the thermoelectric-analyzer is shown in Fig. 6. The crystal analyzed therein is a 12 cm bismuth single crystal alloyed with 0.04 percent Pb and grown at a very slow rate, 0.0003 cm/sec. to illustrate how the lead distributes itself within the crystal. The wavy line record from left to right gives the crystal analysis from front to rear. It is obvious from this record that the lead is pushed to the

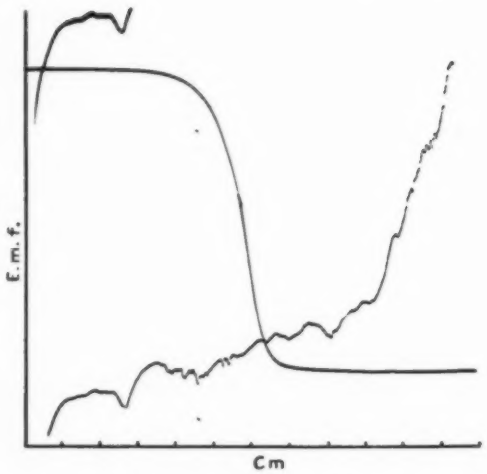

FIG. 6. A typical record obtained with the thermoanalyzer. The wavy line is the thermoelectric analysis of a bismuth crystal, the abscissa representing position along the crystal, the ordinate thermoelectric e.m.f. The smooth line gives the differential thermocouple e.m.f.

rear of the crystal by the process of crystallization and that increasing lead content raises the thermoelectric e.m.f. for this type of crystal, trigonal axis normal to rod. The fine structure on the record gives some idea of the length of inhomogeneity which may be partially resolved. The smooth line record is that produced by the differential thermocouple and gives the temperature distribution as measured by it within the apparatus. The gradient shown here is not as steep as that within the crystal as it is measured by a couple in a glass tube. The temperature difference between chamber A and B is given accurately, however, by the distance between the parallel portions of the record and thus ΔT is determined. Another method is to measure the temperatures of the two emergent water streams with a mercury thermometer.

This record is only one of a large number made on alloyed bismuth crystals, which constitutes a research problem which will shortly be reported in the literature.[4] It serves to illustrate the type of thing which may be done to advantage with an analyzer of this kind.

It is a pleasure to thank Dr. Millikan and Dr. Goetz, who have made the building of this apparatus possible. The latter will publish an article shortly on specific uses for an apparatus of the kind described herein.

[4] To be published shortly in the Physical Review, if possible.

The Shot Effect and Electrical Breakdown in Insulators[1]

F. E. HAWORTH AND R. M. BOZORTH, *Bell Telephone Laboratories*

(Received October 26, 1933)

Measurements are made of the fluctuations in currents passing through insulating materials subjected to high, constant electric fields. Applying the theory of the shot effect to these fluctuations we are able to calculate the average number of elementary charges (electrons or ions) which discharge onto the electrodes as a unit. In glass, this number increases exponentially with the field from about one at low fields to about 10^6 at fields just below breakdown. Considered with respect to various theories offered in explanation of electrical breakdown, our results indicate that the shot effect is caused by "avalanches" of electrons discharging through paths in the material over which breakdown occurs at higher fields, the avalanches increasing in size with the field until the material is ruptured. By making use of the Johnson effect (thermal agitation of electricity) a new and simple method has been worked out for calibrating the amplifier for shot effect measurements.

INTRODUCTION

SINCE Schottky[2] first discovered and interpreted the shot effect in vacuum tube circuits, the theory has been applied to a variety of problems. The fact emerges that studies of the electrical fluctuations or "noise" accompanying many physical phenomena, amplified as may be necessary, are valuable in getting a better insight into the physical processes involved. We have recently measured the fluctuations in currents through insulating materials subjected to high electric fields, and as a result have been led to certain conclusions regarding the nature of electrical breakdown in solids.

METHOD OF MEASUREMENT

The apparatus is shown diagrammatically in Fig. 1 and was similar to that usually used for measurements of the shot effect. The insulator to be tested was at D between the plates of a small condenser. The battery B forced through it a current which also passed through R, the input resistance of the amplifier, so that current fluctuations in the insulator impressed voltage fluctuations upon the grid of the first tube. The amplified fluctuations were impressed at the output upon a vacuum thermocouple connected to a galvanometer, the deflections of the latter thus measuring the fluctuations at the input of the amplifier. By a switching arrangement the same galvanometer was used to measure the magnitude of the conduction current in the insulator. In a telephone receiver substituted for the thermocouple, the fluctuations could be heard as a sharp crackling noise.

FIG. 1. Noise measuring circuit. D is the specimen, B a battery variable from 0 to 1500 volts, R a resistance of 0.1 to 0.5 megohm, Th a thermocouple and G a galvanometer.

The amplifier had a voltage amplification factor of about 10^5, and since the input circuit was of very high impedance, several precautions were necessary to eliminate all sources of noise outside the specimen. The battery B was made up of dry cells to a maximum potential of 1500 volts and had to be very carefully insulated to eliminate small leakage currents. The amplifier and the whole input circuit were carefully shielded. Furthermore, a grounded guard ring or other suitable means was provided on the specimens to eliminate the effects of surface conduction.

The insulator used in most of the experiments was G702EJ Pyrex glass, although measurements

[1] Presented in part before the Committee on Electrical Insulation of the Division of Engineering and Industrial Research of the National Research Council, Boston, November 13, 1931. Also Phys. Rev. **39**, 845 (1932).

[2] W. Schottky, Ann. d. Physik **57**, 541 (1918); **68**, 157 (1922).

were also made on lead glass and mica. The glass specimens were in the form of bubbles blown from small tubes. These little flasks were filled with mercury and immersed in a small beaker of mercury, the mercury surfaces inside and outside being at approximately the same level. Since the edges of the mercury electrodes were separated by glass much thicker than the bubble, the so-called edge effect was eliminated.[3] The mica specimens were in the form of flat sheets, upon which silver was chemically deposited to form electrodes, and these were placed between flat plates with carefully rounded edges.

Since the fluctuations due to the thermal agitation[4] of electrons in the resistance R could not be eliminated, they were allowed for in the measurements. Their presence is actually advantageous since it permits us to eliminate, as will be shown below, factors which are difficult to measure. It was found that a wire-wound resistance or one made of a mixture of xylene and alcohol was suitable for the resistance R, but that an ordinary grid leak could not be used on account of additional voltage fluctuations produced by the passage of current through it.

Several final tests were made to prove that the fluctuations originated in the specimen. The insulator under test was removed and all parts of the circuit so thoroughly insulated that no leakage current could be detected either directly or by the fluctuations such a current would produce. In a second test a resistance of the same order of magnitude as the specimen, but known to give no additional fluctuations upon the passage of current through it, was substituted for the specimen whereupon the fluctuations ceased. They also ceased when one-half the battery was reversed, the potential applied to the insulator being thus reduced to zero while all the other elements of the circuit remained the same. Under these conditions if noise had originated in fluctuations of battery potentials, or in electrical pick-up due to insufficient shielding, it would still have been present.

In order to show that the noise arising in the insulator is not due to electromotive forces arising from local changes in chemical composition, we used a Pyrex glass bulb with a 90 percent sodium amalgam as electrode material in place of mercury. The flask was baked out in a high vacuum and the amalgam introduced without coming in contact with air. With this arrangement any metallic ions plated out of the glass are replaced by ions of the same sort. Also, there is no question here of a discharge taking place in a thin film of gas between the electrode and the glass. We found no difference in the fluctuations due to this change in the electrodes.

Theory

From the power developed in the measuring circuit, we can calculate a quantity which depends upon the sizes of the groups of charges which arrive as a unit at one of the electrodes. The mathematical theory of the shot effect has been worked out in detail, and we follow the presentation of Fry[5] with certain extensions for our special circuit. He derives:

$$S=\bar{\nu}\,\overline{w},$$

where S is the power dissipated in the measuring circuit (in our case in the thermocouple) as a result of the fluctuations, $\bar{\nu}$ is the mean frequency of the electrical impulses resulting from the arrival of groups of charges at the electrodes, and $\overline{w}$ is the mean energy dissipated in the measuring circuit for one impulse. For $\overline{w}$, he derives the relation:

$$\overline{w}=\overline{(ne)^2}\int_0^\infty E(t)i(t)dt,$$

where n is the number of charges in the group, e is the electronic charge, and $E(t)$ and $i(t)$ are the time-functions of the voltage and current in the measuring circuit due to unit charge placed on the electrode at time $t=0$.

But $i_0=\overline{\nu(ne)}$, where i_0 is the mean current through the specimen as measured by a direct-current instrument, giving

$$S=i_0\frac{\overline{(ne)^2}}{\overline{(ne)}}\int_0^\infty E(t)i(t)dt.$$

[3] L. Inge and A. Walther, Archiv f. Electrotechnik **19**, 257 (1928).

[4] J. B. Johnson, Phys. Rev. **32**, 97 (1928).

[5] T. C. Fry, J. Frank. Inst. **199**, 203 (1925).

Simplified by the Carson-MacColl theorem[5] and applied to our special circuit this reduces to:

$$i_D^2 = \frac{ei_0R^2}{\pi}\frac{\overline{n^2}}{\overline{n}}\int_0^\infty \frac{|\gamma|^2 d\omega}{1+R^2C^2\omega^2}.$$

Here i_D is the current in the thermocouple, R is the input resistance, γ is the transfer admittance of the amplifier, ω is 2π times the frequency of the electrical oscillators and C is the total capacity across the input of the amplifier, including the tube capacity, that of the condenser formed by the electrodes and the specimen and the capacities of the connecting wires.

Instead of evaluating this integral by calibrating the amplifier and integrating the resultant curve graphically, we observe that for this circuit Johnson[4] obtained the relation:

$$i_T^2 = \frac{2kTR}{\pi}\int_0^\infty \frac{|\gamma|^2 d\omega}{1+R^2C^2\omega^2},$$

where i_T is the current produced in the thermocouple by the thermal agitation of electrons in the resistance R, k is Boltzmann's constant, T the absolute temperature and C has the same meaning as in the previous equation. Dividing i_D^2 by i_T^2, we have the relation:

$$i_D^2/i_T^2 = (ei_0R/2kT)(\overline{n^2}/\overline{n}),$$

which is independent of C and of the characteristics of the amplifier. In our circuit whenever i_D is present, i_T is also, so that we actually measure $i_D^2+i_T^2$; but by reducing the voltage on the insulator to zero, we measure i_T^2 and can therefore obtain i_D^2 by subtraction.

Before using the relation obtained above we tested it by measuring the shot effect in a two element vacuum tube which was substituted for the insulator. For such a tube n is one and therefore $\overline{n^2}/\overline{n}$ is one, and it should be possible to use the circuit for an accurate measurement of e/k. By using a Western Electric No. 246A vacuum tube as the first amplifier tube and a Davohm wire-wound resistance, it was found that if R was kept below half a megohm the expected value of e/k was precisely that obtained by measurement. In this experiment i_0 was much larger than in the case of insulators and it was necessary to keep it so low that the potential drop through R had a negligible effect upon the grid of the first amplifier tube. We also found that it was necessary to put a high pass filter in the output circuit with a cut-off at about eighty cycles, so that the "flicker effect"[6] and all remnants of sixty cycle pick-up were effectively eliminated.

This method suggests itself as a possible one for determining the ratio e/k with precision. But this ratio is already known with much greater precision than the separate values of e and k and is in fact equal to F/R, the Faraday divided by the gas constant. With this method it is not to be expected that the errors could be kept below the present probable error in e/k which is about 0.01 percent.

As a further check upon our circuit we calibrated the amplifier by means of an oscillator, determining $|\gamma|$ as a function of the frequency. This was plotted and integrated graphically and by use of the result, e was measured from the shot effect in the vacuum tube and k from the resistance noise in R, these values being in substantial agreement with the known values.

Results

Fig. 2 shows a plot made from typical noise data for Pyrex glass. As may be seen, these data scatter badly. However, the fluctuations always increased with increasing potential, and by making many different runs on a given specimen, a good average value for the curve was obtained. Fig. 3 shows the conduction current i_0 as a function of the applied voltage for the sample of Pyrex used for the noise measurements plotted in Fig. 2 and in arbitrary units the conductivity of this specimen as dependent upon voltage.

The quantity $\overline{n^2}/\overline{n}$ is a kind of average value of the number n of unit charges in a single group, and attains values as high as 10^6 in glass. These experimental values may be compared with the values of n predicted by certain theories to be discussed in the next section.

Significance for Breakdown

The experimental results may be considered in relation to various current theories of electrical breakdown. In 1927 it was suggested separately

[6] J. B. Johnson, Phys. Rev. **26**, 71 (1925).

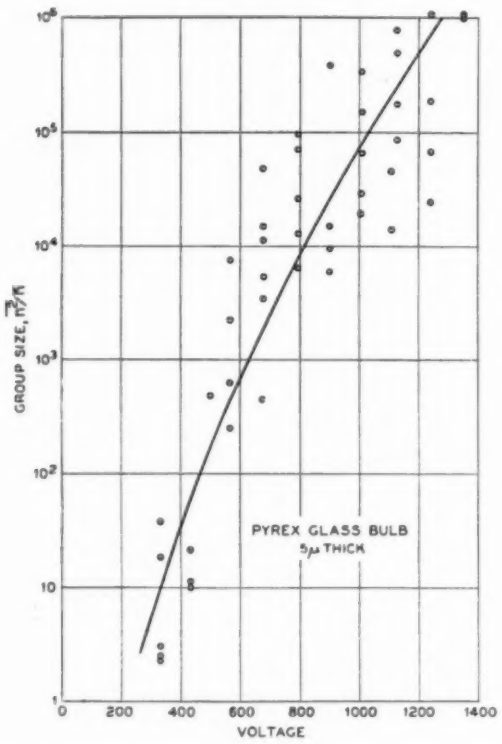

FIG. 2. Group-size as dependent upon voltage. Here n represents the number of charges equal in magnitude to the charge of one electron which discharge onto the electrodes together. The quantity determined by experiments on the shot effect is the ratio of the means, $\overline{n^2}/\overline{n}$.

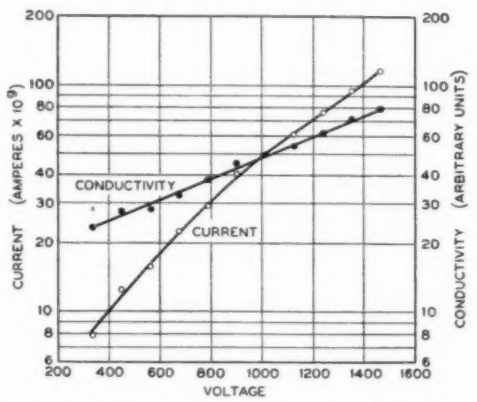

FIG. 3. Conductivity and current as dependent upon voltage for the same glass bulb as used for the data of Fig. 2.

by Joffé,[7] Rogowski[8] and Smekal[9] that in rocksalt, as an example of an insulator, breakdown came about as the result of an excessive positive ion current. According to their views, the mobile Na^+ ions were speeded up by the action of the field until they acquired sufficient energy to free more ions by impact. In Joffé's theory the ions were supposed to be loosened from their normal positions in the crystal lattice; in the theories of the others, the new ions freed were those loosely bound in imperfect parts of the crystal, the imperfect region being enlarged as the ion-current and field-strength increased.

More recently Rogowski,[10] von Hippel[11] and others[12] have proposed that the breakdown is produced by an "avalanche" of electrons due to acceleration by the field and multiplication of the number by ionization by impact. The three chief experimental facts supporting the electron theory as contrasted with the ion theory are: (1) the short time (10^{-7} sec.) of breakdown[13] considered with reference to the low mobility of the ions as compared with the electrons; (2) the lack of dependence of breakdown potential upon the temperature[14] and therefore on the ion current (the resistivity[15] of rocksalt increases by many powers of ten as the temperature decreases from that of the room to that of liquid air, whereas the breakdown voltage does not then increase[16]); (3) the Lichtenberg patterns obtained in the solid by von Hippel, indicating that cumulative ionization is caused by negative carriers.

Our results are readily interpreted in terms of the electronic theory. According to this theory the electrons make a negligible contribution to the ordinary conductivity[17] even at relatively high fields, but when the field is sufficiently high and the ionizations by impact sufficiently great in number a channel is formed from one electrode to

[7] A. Joffé, T. Kurchatoff and K. Sinelnikoff, J. Math. and Physics (M.I.T.) **6**, 133 (1927). A. Joffé, *The Physics of Crystals*, McGraw-Hill, New York, 1928.

[8] W. Rogowski, Archiv f. Elektrotechnik **18**, 123 (1927).

[9] A. Smekal, Archiv f. Elektrotechnik **18**, 525 (1927).

[10] W. Rogowski, Archiv f. Elektrotechnik **23**, 569 (1930).

[11] A. v. Hippel, Zeits. f. Physik **67**, 707 (1931).

[12] L. Rosenkewitsch and C. Sinelnikow, Zeits. f. Physik **73**, 118 (1931); W. Werner, Ann. d. Physik **86**, 95 (1928).

[13] W. Rogowski, E. Flegler and R. Tamm, Archiv f. Elektrotechnik **18**, 479 (1927).

[14] W. Werner, reference 12; A. v. Hippel, reference 11; H. Rochow, Archiv f. Electrotechnik **14**, 361 (1925).

[15] A. Joffé, reference 7 (book), p. 129.

[16] W. Werner, reference 14.

[17] H. Schiller, Ann. d. Physik **83**, 137 (1927).

the other in much the same fashion as in a dense gas. We should expect the average number of electrons in such an avalanche or group of charges to increase exponentially with the field. No very definite statement can be made about the expected number of electrons per avalanche at breakdown; but Rogowski[18] in considering the possibility of observing a single group of charges on a cathode-ray oscillograph has estimated that in air at atmospheric pressure with electrodes 1 cm apart the number of unit charges per group may be of the order of 10^8. We may also estimate that at breakdown the number in a group will be larger by several orders of magnitude than the number of atoms in a single row reaching from one electrode to the other, for at breakdown we expect a channel to be formed within which the lattice is disrupted. In the thin glass used in our experiments the number of atoms in a single row is about 10^5.

The expected law of increase of group size with voltage is confirmed by our experiment, and the above rough estimates of size are at least not inconsistent with our results. On the other hand, the group-size predicted by Joffé's theory is hopelessly small compared to the experimental values. The number per group predicted on his theory is equal to the ratio of the conductivity at the given field to the limiting conductivity at very low fields, and in the case of our glass specimen is less than 10 as shown in Fig. 3.[19]

To express it in another way: if the increase of conductivity in high fields is due to an increase in the number of mobile positive ions produced by ionization by impact, the "*noise*" we should expect from this source alone is orders of magnitude less than that which we actually observe at the highest fields. If the greater part of the noise is caused by the presence of relatively few groups of electrons, the average population of these large groups cannot be determined unless we know the amount of the current carried by the electrons alone. Tests of Faraday's law of electrolytic conduction[20] in similar materials indicate that in high fields the positive ions account for at least 95 to 99 percent of all of the current, so that we may set the upper limit of the fraction carried by electrons as about 10^{-2}. The average number $\bar{n}$, for the *electron* groups corresponding to this fraction is then 10^2 times the previously calculated value of $\overline{n^2}/\bar{n}$, or about 10^8 for our material at fields just below breakdown, as obtained from the final equation above by substituting for i_0 the strength of the electron current. The passage of this number of electrons in a single avalanche recalls the experiments of Inge and Walther[21] and of von Hippel[11] who observed microscopic channels in rocksalt and glass after a field-strength ordinarily sufficient for breakdown was applied for a very short time. It was only after the field was applied for a longer time that the channels were large enough to cause breakdown.

We may conclude that at the present time the experimental data, including those reported here, point to a mechanism of breakdown by electron avalanches, and that the electrical fluctuations which we have observed are due to smaller avalanches insufficient for breakdown.

[18] W. Rogowski, Archiv f. Electrotechnik **25**, 596 (1931).

[19] Recent experiments of G. Just, Zeits. f. Physik **82**, 119 (1933), even throw considerable doubt on the validity of Joffé's determinations of the breakdown of very thin films and indicate that the high values he obtained were due to adsorbed films. It was on the basis of his own results on thin films that Joffé was led to his theory of ionic breakdown.

[20] H. Schiller, reference 17; A. Joffé, Phys. Zeits. d. Sow. **1**, 176 (1932).

[21] L. Inge and A. Walther, Archiv f. Electrotechnik **24**, 259 (1930).

Unsteady Flow of Fluids in Oil Reservoirs

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(Received October 30, 1933)

This paper is an analysis of the unsteady flow of a compressible fluid flowing radially to a well in a sand formation. The phenomenon of unsteady flow occurs as a result of fluid expansion. When the pressure in the formation is lowered, the fluids therein expand and the increase in volume imparts motion to the fluid which flows towards the region of lowest pressure in the formation. This process is continuous in the reservoir and extends further away from the well with increased production. By the "equation of continuity," the solution for two specific cases of unsteady flow are derived. The first of these is that in which the fluid from a sand reservoir of limited size flows to a well in which the pressure at the level of the producing sand always remains constant. The variation of the pressure gradient, the rate of production, and the cumulative production with respect to time are given in Eqs. (11), (24), (29) and (30). The second case is that in which the flow of fluid to a well is such that the rate of production at the well is always constant. This case is derived by the assumption that the cylindrical body of sand, which is influenced by the well, is subject to a steady depletion of fluid, and in order that the rate remain constant at the well, fluid must flow into the reservoir from some extraneous source in increasing amounts. Eventually, however, the rate of flow of fluid into the reservoir becomes equal to the rate at which fluid is withdrawn from the well and steady flow is established in the sand. The equations for the pressure gradient and the decline of pressure at the well with respect to time are (39), (52) and (56).

INTRODUCTION

FLUIDS encountered in oil reservoirs are compressible, and because of their expansion during the course of production, the flow of these fluids to wells is unsteady. When the well is opened, the pressure at the well bore is lowered, causing the fluid near the well to expand and flow toward the well. The loss of fluid from the reservoir lowers the pressure in the more distant portion of the reservoir, permitting the fluid in those portions to expand and flow to the well. Thus, the area around the well affected by drainage is continuously enlarging, and the pressure and velocity of the fluid is changing continuously at all points in the reservoir. This condition is characteristic of the unsteady state of flow.

Under certain circumstances, the equations for steady flow are useful approximations. This is true because the rate of change of the pressure gradients in the later periods of production is relatively small. The analysis of steady flow of fluids through sand formations has been developed by different investigators.[1, 2, 3]

EQUATION OF CONTINUITY

In order to develop the analysis for the unsteady flow of fluids through a sand, certain assumptions must be made. These are as follows:

(1) The permeability, porosity, and thickness of a sand are uniform throughout that portion of the formation affected by a well.

(2) The well bore is cylindrical and penetrates the entire thickness of sand.

(3) The mixture of oil and gas behaves as a homogeneous fluid, and the velocity of flow at any point in the sand is directly proportional to the pressure drop per unit of length along the path of flow.

(4) The density of the fluid within the sand is expressed by the equation

$$\rho = \rho_w \epsilon^{c(P-P_w)}, \tag{1}$$

where ρ_w is the density of the fluid at the well, P_w the pressure at the well face, and c the compressibility of the fluid.

The exponential expression for density is an assumption which has been adopted for convenience. It is applicable for a slightly compressible fluid[4] since it reduces to

$$\rho = \rho_w[1+c(P-P_w)],$$

[1] Schlichter, U. S. G. S., Nineteenth Annual Report, 1897–8.

[2] Morris Muskat, Physics **2**, 329 (1932).

[3] H. D. Wilde, Jr., and T. V. Moore, Oil Weekly, December 5, 1932.

[4] Lamb, *Hydrodynamics*, Cambridge University Press, p. 6, 1916.

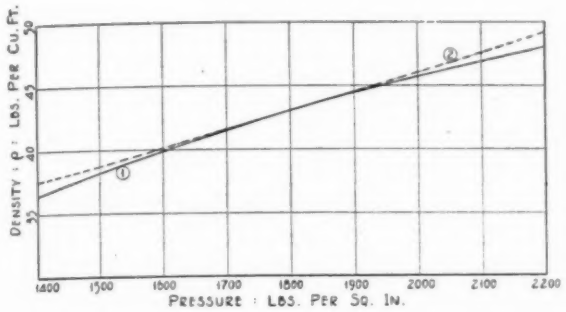

FIG. 1. Density-pressure curves. (1) Calculated from solubility and gas laws; (2) calculated from equation $\rho=\rho_w\epsilon^{c(P-P_w)}$.

when c is small. Furthermore, for a fluid of relatively large compressibility, it gives a fairly close approximation over a wide pressure range as shown in Fig. 1.[5]

The equation of continuity, which is primarily a fluid balance over an infinitesimal element of sand, is expressed by the equation

$$\frac{\partial(\rho u)}{\partial x}+\frac{\partial(\rho v)}{\partial y}=-\frac{\phi}{\phi'}\frac{\partial\rho}{\partial\theta}, \tag{2}$$

where u and v are the component velocities of the fluid which flows parallel to the plane XOY and toward the origin, Fig. 2. The constant, ϕ/ϕ', is the ratio of the volume porosity of sand to its surface porosity and θ is time.

The component velocities of the fluid may be expressed as

$$u=-\frac{K}{\phi'}\frac{\partial P}{\partial x} \quad \text{and} \quad v=-\frac{K}{\phi'}\frac{\partial P}{\partial y}, \tag{3}$$

where K is the permeability of the sand.

Therefore,

$$\rho u=-\rho(K/\phi')(\partial P/\partial x),$$

but

$$\partial\rho/\partial x=c\rho_w\epsilon^{c(P-P_w)}\partial P/\partial x=c\rho\partial P/\partial x;$$

then

$$\rho\mu=-\frac{K}{\phi' c}\frac{\partial\rho}{\partial x} \quad \text{and} \quad \rho v=-\frac{K}{\phi' c}\frac{\partial\rho}{\partial y}.$$

The substitution of these values in Eq. (2) gives

$$(\partial^2\rho/\partial x^2+\partial^2\rho/\partial y^2)\alpha^2=\partial\rho/\partial\theta, \tag{4}$$

where $\alpha^2=K/c\phi$.

Because this equation is similar to that for the unsteady flow of heat through a homogeneous solid, α^2 may be referred to as the "hydraulic diffusivity," as comparable to the "thermal diffusivity" in the heat equation.[6]

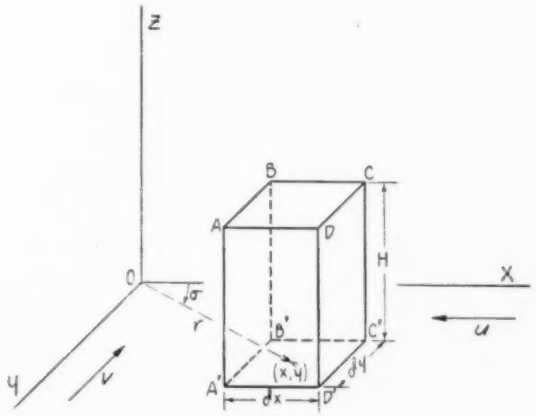

FIG. 2.

For the radial flow of fluid to the well, this equation is transformed so that

$$(\partial^2\rho/\partial r^2+(1/r)\partial\rho/\partial r)\alpha^2=\partial\rho/\partial\theta \tag{5}$$

and the solution of this equation is

$$\rho=\sum_{n=1}^{\infty}[A_nJ_0(\beta_nr)+B_nY_0(\beta_nr)]\epsilon^{-\beta_n^2\alpha^2\theta}. \tag{6}$$

In this expansion $J_0(\beta_nr)$ and $Y_0(\beta_nr)$ are Bessel functions of zero order. The second kind of Bessel, $Y_0(\beta_nr)$, is the Weber-Schläfi[7] function. Furthermore, A_n, B_n, and β_n in Eq. (6) are constants to be determined from the conditions imposed on the problem. The possibility of this expansion[8] and that the series can be integrated term by term is assumed for the present.

Associated with these Bessel functions are the recurrence formulae[9] which are applicable in this analysis.

$$d\{z^nJ_n(z)\}/dz=z^nJ_{n-1}(z), \tag{7}$$

$$d\{z^{-n}J_n(z)\}/dz=-z^nJ_{n+1}(z), \tag{8}$$

$$d\{z^nY_n(z)\}/dz=z^nY_{n-1}(z), \tag{9}$$

$$d\{z^{-n}Y_n(z)\}/dz=-z^nY_{n+1}(z). \tag{10}$$

[5] Moore, Schilthuis and Hurst, Oil Weekly, **69**, May 21, 1933.

[6] Carslaw, *The Conduction of Heat*, Macmillan, p. 8, 1921.

[7] Numerical tables for both kinds of Bessel functions are given by Watson, *Theory of Bessel Functions*, Camb. University Press, 1922.

[8] Hobson, London Proc. Math. Soc., [2] **7** (1909).

[9] Watson, reference 7, 2.12 and 3.56.

Case I. Constant Well Pressure

The limits for the case when the well pressure remains constant and the depletion of fluid takes place in a finite cylindrical sand reservoir, concentric with the well, are as follows:

$$\left.\begin{aligned} &r=a, \quad P=P_w \\ &r=b, \quad \lim_{r\to b}(\partial P/\partial r)=0 \end{aligned}\right\} 0<\theta<\infty$$

and $\theta=0$, $P=P_R$. From Eq. (1), these conditions may be interpreted in terms of density, and a plot illustrating these limits is shown in Fig. 3. It is observed that the field is limited in extent by the assumption that the pressure slope is zero at the radius b, and therefore no fluid can flow across this boundary.

Let

$$\rho=(\rho_R-\rho_w)\Delta+\rho_w, \tag{11}$$

where ρ_w and ρ_R are constants. Then by Eqs. (5) and (6)

$$\Delta=\sum_{n=1}^{\infty}\left[A_n J_0(\beta_n r)+B_n Y_0(\beta_n r)\right]\epsilon^{-\beta_n^2\alpha^2\theta}. \tag{12}$$

As a simplification of this problem, let

$$V_0(\beta_n r)=Y_0(\beta_n a)J_0(\beta_n r)-J_0(\beta_n a)Y_0(\beta_n r), \tag{13}$$

then

$$\Delta=\sum_{n=1}^{\infty} M_n V_0(\beta_n r)\epsilon^{-\beta_n^2\alpha^2\theta}, \tag{14}$$

where $A_n=M_n Y_0(\beta_n a)$ and $B_n=-M_n J_0(\beta_n a)$. Therefore,

$$\lim_{r\to a}\Delta=\sum_{n=1}^{\infty} M_n V_0(\beta_n a)\epsilon^{-\beta_n^2\alpha^2\theta}=0$$

and then by Eq. (11) $\rho=\rho_w$, when $r=a$.

The differentiation of the series expansion, Eq. (14), with respect to r is the equation

$$\partial\Delta/\partial r=-\sum_{n=1}^{\infty}\beta_n M_n V_1(\beta_n r)\epsilon^{-\beta_n^2\alpha^2\theta},$$

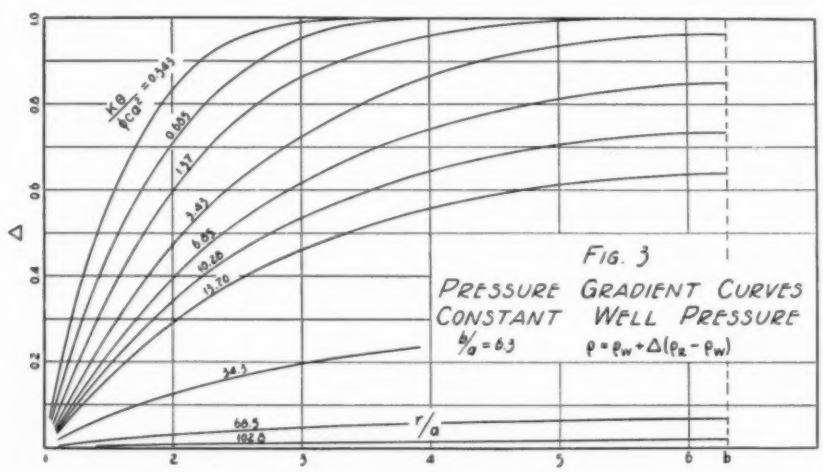

FIG. 3.

where

$$V_1(\beta_n r) = Y_0(\beta_n a)J_1(\beta_n r) - J_0(\beta_n a)\,Y_1(\beta_n r) \tag{15}$$

by the recurrence formulae Eqs. (8) and (10). If

$$\lim_{r\to b}\frac{\partial \Delta}{\partial r} = -\sum_{n=1}^{\infty}\beta_n M_n V_1(\beta_n b)\epsilon^{-\beta_n^2\alpha^2\theta} = 0$$

the limit at the outer boundary b is satisfied if we assume that each term in the series expansion is equal to zero. Then, $V_1(\beta_n b)$ is equal to zero or

$$J_0(\beta_n a)/Y_0(\beta_n a) = J_1(\beta_n b)/Y_1(\beta_n b) \tag{16}$$

and Eq. (16) establishes the many values of the root β_n in the expansion from $n=1$ to $n=\infty$.

Finally, in order to establish the limit when time is zero it is necessary that

$$\lim_{\theta\to 0}\Delta = M_1V_0(\beta_1 r) + M_2V_0(\beta_2 r) + M_3V_0(\beta_3 r) + \cdots = 1 \tag{17}$$

when $a < r \leq b$.

The coefficients M_1, M_2, etc., may be determined by the following method:

Let $V_0(\tau r)$ and $V_0(\omega r)$ be any two Bessel functions whose roots are not equal. Then,

$$r^2d^2\{V_0(\tau r)\}/dr^2 + rd\{V_0(\tau r)\}/dr + \tau^2r^2V_0(\tau r) = 0$$

or

$$(1/r)(d/dr)[rd\{V_0(\tau r)\}/dr] + \tau^2V_0(\tau r) = 0.$$

Likewise,

$$(1/r)(d/dr)[rd\{V_0(\omega r)\}/dr] + \omega^2V_0(\omega r) = 0.$$

By combining these two equations, we have

$$(\omega^2-\tau^2)rV_0(\tau r)\,V_0(\omega r) = V_0(\omega r)\frac{d}{dr}\left[r\frac{d\{V_0(\tau r)\}}{dr}\right] - V_0(\tau r)\frac{d}{dr}\left[\frac{rd\{V_0(\omega r)\}}{dr}\right].$$

The integration of both sides of this equation with respect to r from the limits a to b gives

$$(\omega^2-\tau^2)\int_a^b rV_0(\tau r)\,V_0(\omega r)dr = \left[rV_0(\omega r)\frac{d\{V_0(\tau r)\}}{dr} - rV_0(\tau r)\frac{d\{V_0(\omega r)\}}{dr}\right]\Bigg|_a^b.$$

Since $V_1(\tau b)$, $V_1(\omega b)$, $V_0(\tau a)$, and $V_0(\omega a)$ are equal to zero by the conditions already established then,

$$\int_a^b rV_0(\tau r)\,V_0(\omega r)dr = 0 \tag{18}$$

when $\tau \neq \omega$.

If, however, the two roots are equal, this integral may be established as follows:

$$(1/r)(d/dr)[rd\{V_0(\tau r)\}/dr] + \tau^2V_0(\tau r) = 0.$$

This equation multiplied by $2r^2d\{V_0(\tau r)\}/dr$ gives

$$(d/dr)[rd\{V_0(\tau r)\}/dr]^2 + \tau^2r^2(d\{V_0^2(\tau r)\}/dr) = 0.$$

The integration of this equation with respect to r from the limits a to b is

$$\int_a^b rV_0^2(\tau r)dr = (1/2\tau^2)[(rd\{V_0(\tau r)\}/dr)^2 + (\tau rV_0(\tau r))^2]\Big|_a^b$$

$$= \tfrac{1}{2}\{[bV_0(\tau b)]^2 - [aV_1(\tau a)]^2\}$$

since $V_1(\tau b)$ and $V_0(\tau a)$ are equal to zero. However,

$$V_1(\tau a) = Y_0(\tau a)J_1(\tau a) - J_0(\tau a)Y_1(\tau a)$$

is comparable to

$$Y_n(z)J_{n+1}(z) - J_n(z)Y_{n+1}(z) = 2/\pi z \tag{19}$$

given by Watson.[10] Therefore, $V_1(\tau a) = 2/\pi\tau a$ and

$$\int_a^b r V_0^2(\tau r)dr = (1/2\tau^2\pi^2)\{[\pi\tau b V_0(\tau b)]^2 - 4]\}. \tag{20}$$

Another definite integral

$$\int_a^b r V_0(\tau r)dr = -2/\pi\tau^2 \tag{21}$$

may be derived by the recurrence formulae and Eq. (19).

If then Eq. (17) is multiplied through by $rV_0(\beta_n r)$ where β_n is a root appearing in the series, and each term is integrated with respect to r from the limits a to b,

$$M_n = \int_a^b r V_0(\beta_n r)dr \Big/ \int_a^b r V_0^2(\beta_n r)dr$$

by virtue of Eq. (18).

Furthermore, by the substitution of Eqs. (20) and (21) in this formula

$$M_n = 4\pi/\{4 - [\pi\beta_n b V_0(\beta_n b)]^2\} \tag{22}$$

and

$$\Delta = 4\pi \sum_{n=1}^{\infty} \frac{V_0(\beta_n r)\epsilon^{-\beta_n^2\alpha^2\theta}}{\{4 - [\pi\beta_n b V_0(\beta_n b)]^2\}}. \tag{23}$$

If, however, we adopt the well radius, a, as the unit of length in Eq. (23), and let $\beta_n = \beta_n'/a$, $r' = r/a$, and $b' = b/a$ this equation becomes

$$\Delta = \sum_{n=1}^{\infty} M_n' V_0(\beta_n' r')\epsilon^{-\beta_n'^2\alpha^2\theta/a^2}, \tag{24}$$

where $M_n' = 4\pi/\{4 - [\pi\beta_n' b' V_0(\beta_n' b')]^2\}$, and $J_0(\beta_n')/Y_0(\beta_n') = J_1(\beta_n' b')/Y_1(\beta_n' b')$. (25)

Production rate

Production rate is equal to the product of the velocity of fluid entering the well and the area of the surface of the well bore, or

$$q_w = 2\pi a H \phi' \mu_a, \tag{26}$$

where H is the thickness of sand, and μ_a the radial velocity of the fluid at the well. Further,

$$\mu_a = \frac{K}{\phi'} \lim_{r\to a} \frac{\partial P}{\partial r} = \frac{K}{\phi' c \rho_w} \lim_{r\to a} \frac{\partial \rho}{\partial r} \qquad \text{and} \qquad \lim_{r\to a} \frac{\partial \rho}{\partial r} = (\rho_R - \rho_w) \lim_{r\to a} \frac{\partial \Delta}{\partial r}.$$

If we assume that each term in the series expansion Eq. (23) may be differentiated with respect to r in the interval a to b, then

[10] Watson reference 7, p. 77.

$$\frac{\partial \Delta}{\partial r} = -\sum_{n=1}^{\infty} M_n \beta_n V_1(\beta_n r) \epsilon^{-\beta_n^2 \alpha^2 \theta} \qquad \text{and} \qquad \lim_{r \to a} \frac{\partial \Delta}{\partial r} = -(2/\pi a) \sum_{n=1}^{\infty} M_n \epsilon^{-\beta_n^2 \alpha^2 \theta}$$

since $V_1(\beta_n a) = 2/\pi \beta_n a$. Furthermore by substituting $\beta_n = \beta_n'/a$ then

$$\lim_{r \to a} \frac{d\Delta}{\partial r} = -\frac{2}{\pi a} \sum_{n=1}^{\infty} M_n' \epsilon^{-\beta_n'^2 \alpha^2 \theta / a^2}$$

and

$$q_w = -[4HK(\rho_R - \rho_w)/c\rho_w] \sum_{n=1}^{\infty} M_n' \epsilon^{-\beta_n'^2 \alpha^2 \theta / a^2}. \tag{27}$$

The rate of fluid produced at the well can be determined as the volume it would occupy at the initial formation pressure instead of well pressure, since

$$q_w \rho_w = q_R \rho_R. \tag{28}$$

Therefore,

$$\frac{q_R \rho_R C}{KH(\rho_R - \rho_w)} = -4 \sum_{n=1}^{\infty} M_n' \epsilon^{-\beta_n' \alpha^2 \theta / a^2} \tag{29}$$

or

$$q_R C / KH[1 - \epsilon^{-c(P_R - P_w)}] = F(b/a,\ \alpha^2 \theta / a^2).$$

The reciprocal of this argument *versus* time is represented as a family of curves in Fig. 4.

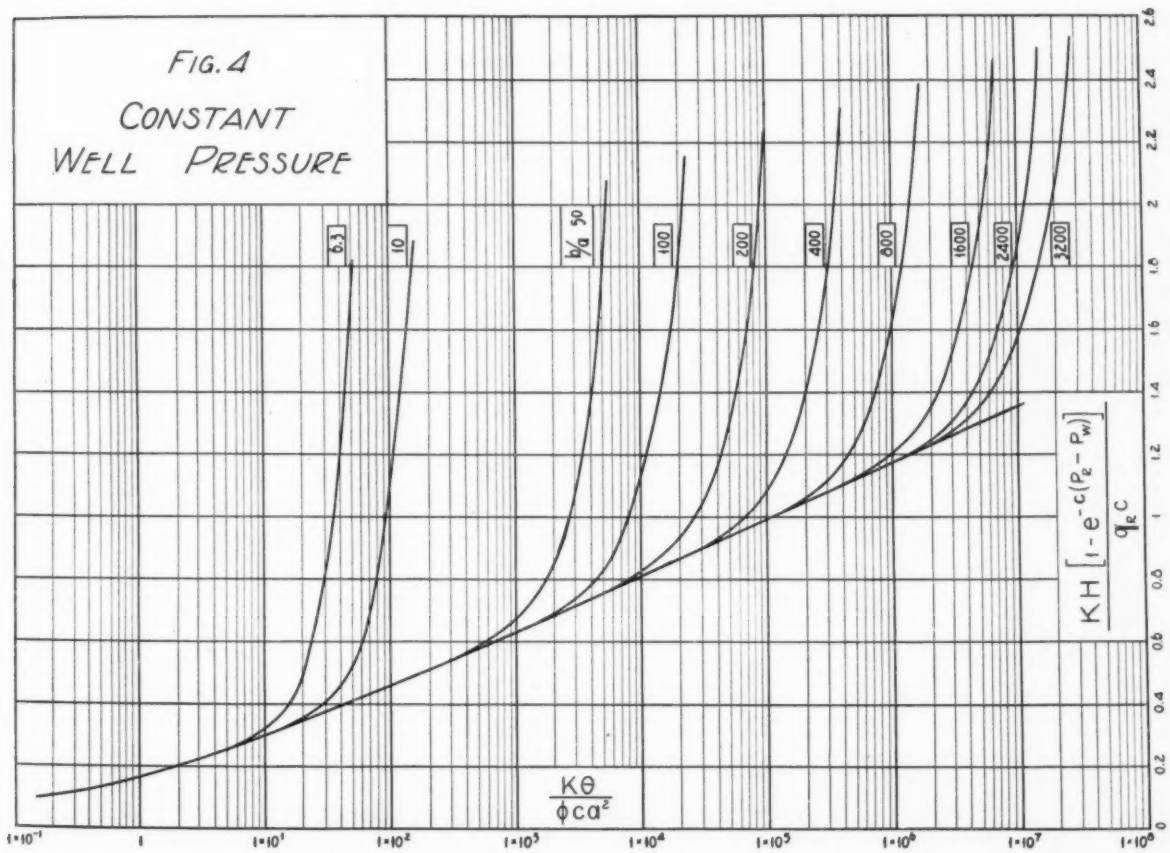

FIG. 4.

Cumulative production

Since cumulative production is the integration of the rate with respect to time, it is expressed as

$$Q_R = \int_0^\theta q_R d\theta.$$

Therefore, the integration of Eq. (27) with respect to time and the substitution of (28) gives the formula

$$\frac{Q_R \rho_R \alpha^2 c}{KHa^2(\rho_R - \rho_w)} = -4 \sum_{n=1}^{\infty} \frac{M_n'(1-\epsilon^{-\beta_n'^2 a^2\theta/a^2})}{\beta_n'^2} \tag{30}$$

or

$$Q_R/H\phi a^2[1-\epsilon^{-c(P_R-P_w)}] = F_1(b/a,\ \alpha^2\theta/a^2).$$

The cumulative production may be determined graphically when the pressure gradient is established in the sand. This is given by the equation

$$\frac{Q_R}{H\phi a^2[1-\epsilon^{-c(P_R-P_w)}]} = \frac{2\pi}{a^2}\int_a^b r(1-\Delta)dr. \tag{31}$$

Furthermore, by means of this equation, the total cumulative production of fluid from a reservoir over an infinite time can be calculated.

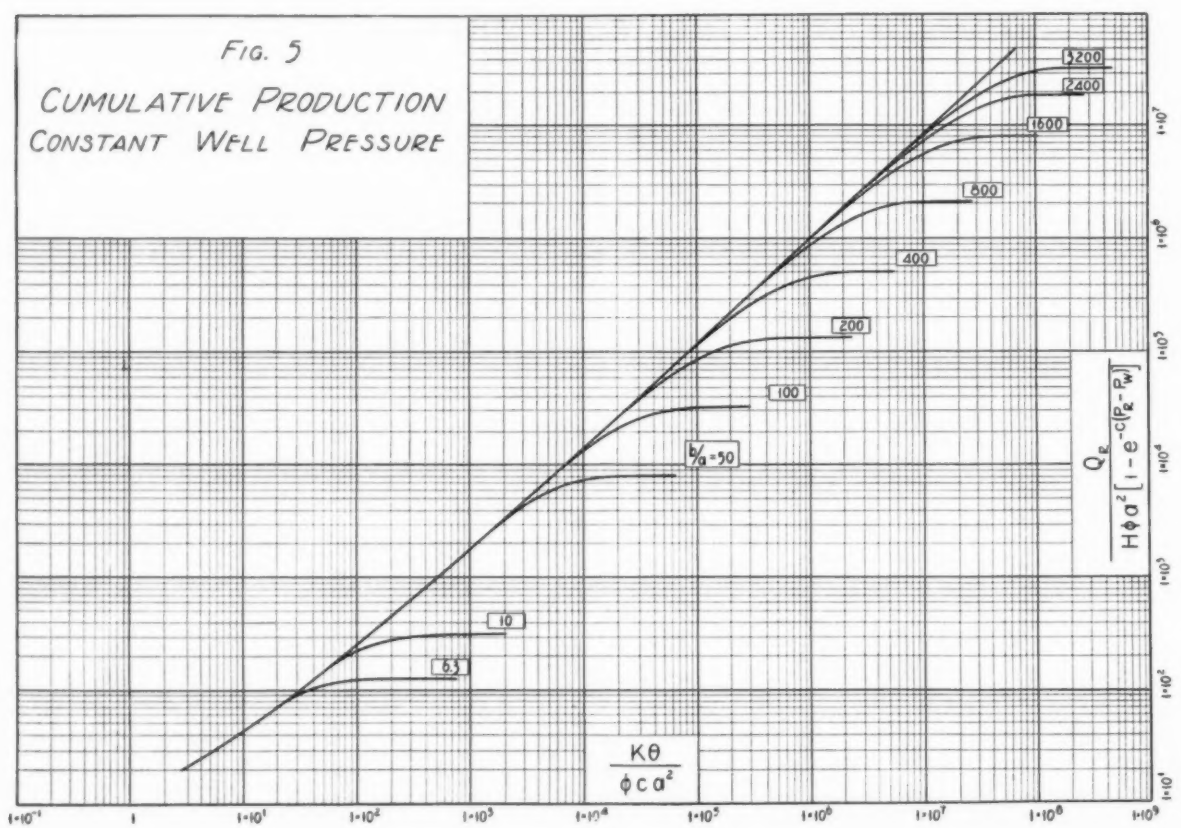

FIG. 5.

Since $\lim_{\theta\to\infty}(1-\Delta)=1$ therefore,

$$\frac{Q_R}{Hk\phi a^2[1-\epsilon^{-c(P_R-P_w)}]}=\frac{2\pi}{a^2}\int_0^b r\,dr=\pi(b'^2-1),$$

which is the asymptote that the corresponding b' curve in Fig. 5 approaches as a limit.

Case II. Constant Production Rate

In order to maintain constant rate of flow at a well, it is necessary that the slope of the pressure gradient at the well face remain constant at all times.

This case is derived by the assumption that the unsteady flow of fluids in a reservoir to a well depletes the sand of fluid to such an extent that in order to maintain the rate constant at the well, fluids must flow across the outer boundary into the reservoir in increasing amounts. Eventually, however, this rate of flow of fluid into the reservoir is the same as the rate of production from the well and steady flow is established in the sand.

Let

$$\rho=(\rho_R-\rho_\infty)\Delta+\rho_\infty, \tag{32}$$

where ρ_∞ is the density of the fluid at the well in infinite time, and it is assumed that

$$\Delta=\xi(r,\theta)+\eta(r). \tag{33}$$

Since

$$(\partial^2\Delta/\partial r^2+(1/r)\partial\Delta/\partial r)\alpha^2=\partial\Delta/\partial\theta,$$

therefore

$$(\partial^2\xi/\partial r^2+(1/r)\partial\xi/\partial r)\alpha^2=\partial\xi/\partial\theta. \tag{34}$$

and

$$d^2\eta/dr^2+(1/r)d\eta/dr=0. \tag{35}$$

The solution for (34) is as before,

$$\xi=\sum_{n=1}^{\infty}[A_nJ_0(\lambda_n r)+B_nY_0(\lambda_n r)]\epsilon^{-\lambda_n^2\alpha^2\theta} \tag{36}$$

and for (35), it may be shown to be,

$$\eta=C\ln r+D. \tag{37}$$

This equation expresses the conditions of steady flow since the limit of ξ is zero when time approaches infinity.

The limits for this problem are as follows:

$$\left.\begin{array}{l}\lim_{r\to a}\dfrac{\partial\Delta}{\partial r}=\text{constant}\\[2ex]\lim_{r\to b}\Delta=1\end{array}\right\}0\le\theta\le\infty \quad \text{and} \quad \theta=0, \quad \Delta=1, \quad a\le r\le b.$$

The gradients for this case are shown in Fig. 6.

Steady state

If we substitute the limits for the steady state in Eq. (32), namely,

$$r=a, \quad \rho=\rho_\infty \quad \text{and} \quad r=b, \quad \rho=\rho_R,$$

then

$$\rho_R=(\rho_R-\rho_\infty)(C\ln b+D)+\rho_\infty \quad \text{and} \quad \rho_\infty=(\rho_R-\rho_\infty)(C\ln a+D)+\rho_\infty.$$

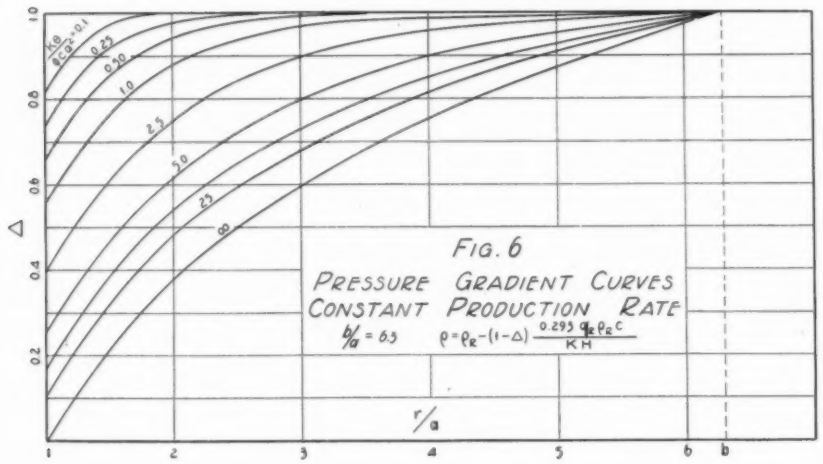

FIG. 6.

Therefore,

$$\eta = \ln (r/a)/\ln (b/a). \tag{38}$$

The rate of production at infinite time is the equation

$$q_\infty = \frac{2\pi aHK}{c\rho_\infty} \lim_{r\to a} \frac{\partial \rho}{\partial r} \qquad \text{or} \qquad q_R = \frac{2\pi aHK}{c\rho_R} \lim_{r\to a} \frac{\partial \rho}{\partial r}$$

if the fluid be measured at the original reservoir pressure. However,

$$\lim_{r\to a} (\partial\rho/\partial r) = (\rho_R - \rho_\infty) \lim_{r\to a} (d\eta/dr) = (\rho_R - \rho_\infty)/a \ln (b/a)$$

and

$$\rho_\infty = \rho_R - [q_R\rho_R c \ln (b/a)]/(2\pi HK).$$

Therefore, if ρ_∞ is substituted in Eq. (32),

$$\rho = \rho_R - [(1-\Delta)q_R\rho_R c \ln (b/a)]/(2\pi HK). \tag{39}$$

Unsteady state

The necessary limits for the unsteady state solution of this problem are as follows: Since

$$\Delta = \xi + \eta \tag{33}$$

and

$$\lim_{r\to a} \frac{\partial \Delta}{\partial r} = \lim_{r\to a} \frac{\partial \xi}{\partial r} + \lim_{r\to a} \frac{\partial \eta}{\partial r}, \qquad \text{then} \qquad \lim_{r\to a} \frac{\partial \Delta}{\partial r} = \lim_{r\to a} \frac{\partial \eta}{\partial r} = \text{constant}$$

if

$$\lim_{r\to a} \frac{\partial \xi}{\partial r} = 0, \tag{40}$$

which is the requirement that the pressure slope at all times is constant at the well.

Furthermore, since

$$\lim_{r\to b} \Delta = 1, \qquad 0 \le \theta \le \infty \qquad \text{and} \qquad \lim_{r\to b} \eta = 1, \qquad \theta = \infty$$

therefore

$$\lim_{r\to b} \xi = 0. \tag{41}$$

Finally, since $\Delta = 1$ when time is zero, then

$$\lim_{\theta \to 0} \xi = 1 - \ln (r/a)/\ln (b/a) = -\ln (r/b) \ln (b/a). \tag{42}$$

If we let

$$U_0(\lambda_n r) = Y_0(\lambda_n b) J_0(\lambda_n r) - J_0(\lambda_n b) Y_0(\lambda_n r)$$

in Eq. (36), then

$$\xi = \sum_{n=1}^{\infty} N_n U_0(\lambda_n r) \epsilon^{-\lambda_n^2 \alpha^2 \theta}, \tag{43}$$

where $A_n = N_n Y_0(\lambda_n b)$ and $B_n = -N_n J_0(\lambda_n b)$. Therefore the limit of ξ as r approaches b is zero and the condition of (41) is satisfied.

Furthermore,

$$\partial \xi / \partial r = -\sum_{n=1}^{\infty} N_n \lambda_n U_1(\lambda_n r) \epsilon^{-\lambda_n^2 \alpha^2 \theta}, \qquad \text{where} \qquad U_1(\lambda_n r) = Y_0(\lambda_n b) J_1(\lambda_n r) - J_0(\lambda_n b) Y_1(\lambda_n r)$$

by recurrence formulae (8) and (10).

Then, if

$$\lim_{r \to a} \frac{\partial \xi}{\partial r} = -\sum_{n=1}^{\infty} N_n \lambda_n U_1(\lambda_n a) \epsilon^{-\lambda_n^2 \alpha^2 \theta} \tag{44}$$

and we assume that each term in the series expansion is equal to zero, the condition of (40) is fulfilled if $U_1(\lambda_n a) = 0$. Or,

$$J_1(\lambda_n a)/Y_1(\lambda_n a) = J_0(\lambda_n b)/Y_0(\lambda_n b). \tag{45}$$

This equation establishes the values of λ_n from $n = 1$ to $n = \infty$.

For time equal to zero

$$-\ln (r/b)/\ln (b/a) = N_1 U_0(\lambda_1 r) + N_2 U_0(\lambda_2 r) + N_3 U_0(\lambda_3 r) + \cdots. \tag{46}$$

The values of N_1, N_2, etc., may be derived by a method similar to the one used in the preceding case.

It can be shown that

$$\int_a^b r U_0(\tau r) U_0(\omega r) dr = 0 \tag{47}$$

when $\tau \neq \omega$, and

$$\int_a^b r U_0^2(\tau r) dr = (1/2\tau^2\pi^2) \{4 - [\tau a \pi U_0(\tau a)]^2\} \tag{48}$$

when the roots are equal.

Another definite integral, which is applicable in this analysis, is

$$\int_a^b \ln (r/b) U_0(\tau r) r dr = -U_0(\tau a)/\tau^2. \tag{49}$$

This integration is derived by the recurrence formulae and the conditions imposed on the problem.

If Eq. (46) is multiplied through by $r U_0(\lambda_n r)$, where λ_n is a root appearing in the series, and each term integrated with respect to r from the limits a to b, then

$$N_n = -\frac{1}{\ln (b/a)} \frac{\int_a^b \ln (r/b) U_0(\lambda_n r) r dr}{\int_a^b r U_0^2(\lambda_n r) dr}$$

by virtue of Eq. (47). By substituting (48) and (49) in this formula

$$N_n = 2\pi^2 U_0(\lambda_n a)/\ln (b/a) \{4 - [\lambda_n a \pi U_0(\lambda_n a)]^2\}. \tag{50}$$

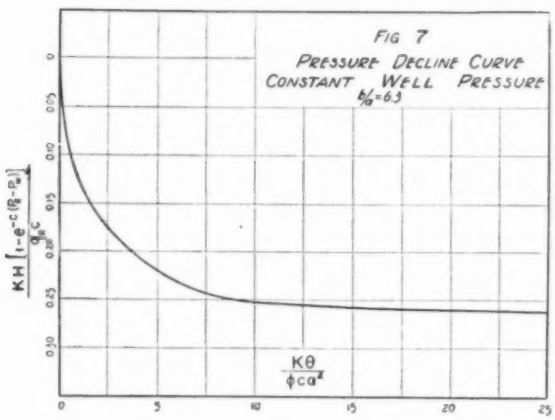

FIG. 7.

The final form is the expression

$$\xi = \frac{2\pi^2}{\ln (b/a)} \sum_{n=1}^{\infty} \frac{U_0(\lambda_n a) U_0(\lambda_n r) \epsilon^{-\lambda_n^2 \alpha^2 \theta}}{\{4 - [\lambda_n a \pi U_0(\lambda_n a)]^2\}} \tag{51}$$

and

$$\Delta = \sum_{n=1}^{\infty} N_n U_0(\lambda_n r) \epsilon^{-\lambda_n^2 \alpha^2 \theta} + \ln (r/a)/\ln (b/a). \tag{52}$$

The variation of well pressure *versus* time may be determined by Eqs. (39) and (52). Therefore,

$$p_w = p_R - \frac{q_R \rho_R c \ln (b/a)}{2\pi IIK} \lim_{r \to a} (1 - \Delta). \tag{53}$$

However,

$$1 = \sum_{n=1}^{\infty} N_n U_0(\lambda_n r) + \ln (r/a)/\ln (b/a) \tag{54}$$

for $a \leq r \leq b$, when $\theta = 0$. So by combining Eqs. (52) and (54) for corresponding roots, we have

$$\lim_{r \to a} (1 - \Delta) = \sum_{n=1}^{\infty} N_n U_0(\lambda_n a)(1 - \epsilon^{-\lambda_n^2 \alpha^2 \theta}).$$

If as in the preceding case, the well radius, a, is taken as a unit length, then

$$\lim_{r \to a} (1 - \Delta) = \frac{2\pi^2}{\ln (b')} \sum_{n=1}^{\infty} \frac{U_0^2(\lambda_n')(1 - \epsilon^{-\lambda_n'^2 \alpha^2 \theta/a^2})}{\{4 - [\lambda_n' \pi U_0(\lambda_n')]^2\}} \tag{55}$$

and

$$J_1(\lambda_n')/Y_1(\lambda_n') = J_0(\lambda_n' b')/Y_0(\lambda_n' b').$$

Therefore, by substituting Eq. (55) in (53) and simplifying

$$\frac{KII[1 - \epsilon^{-c(P_R - P_w)}]}{q_R c} = \pi \sum_{n=1}^{\infty} \frac{U_0^2(\lambda_n')(1 - \epsilon^{-\lambda_n'^2 \alpha^2 \theta/a^2})}{\{4 - [\lambda_n' \pi U_0(\lambda_n')]^2\}} \tag{56}$$

and P_w is now the variable well pressure.

The decline curve for well pressure *versus* time is shown for a particular sand reservoir in Fig. 7.

The author is indebted to W. K. Lewis, of the Department of Chemical Engineering, Massachusetts Institute of Technology, and H. D. Wilde, Jr., in charge of production research at the Humble Oil & Refining Company, for the valuable suggestions which they have contributed during the course of this work. Furthermore, the author wishes to acknowledge the cooperation of T. V. Moore and R. J. Schilthuis whose kind assistance has made possible the application of this theory[5] to the oil industry.

A Magneto-Optic Method of Determining the Vitamin Content of Various Substances

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In this investigation, the magneto-optic apparatus was used, but it was modified to some extent from the original apparatus used by Allison. The modifications included a mercury vapor arc and a monochromator to furnish a steady source of monochromatic light, and a photoelectric cell and amplifier circuit to read the minima. The apparatus gave a distinct minimum, at 32.9 on the electrical path scale, for all substances tested which contained vitamin A but did not show this minimum for similar substances in which this vitamin was lacking. Pure carotene did not give this minimum. Pure carotene after irradiation with ultraviolet light, however, did give it.

INTRODUCTION

EVER since the discovery of vitamins, much research has been done in an effort to isolate the vitamin from the food containing it and to find the vitamin content of various foods. In order to determine the vitamin content of foods, the biologists have used the feeding test method but this method has been rather slow and hard to control accurately. During the last few years, attempts have been made to find a more rapid method than the biological for finding this quantity. Chemists have worked to find the chemical constitution of the vitamin itself and so isolate the vitamin from the food in which it was found. The physicist has used different methods among which the colorimetric and spectrographic are the outstanding.

The purpose of this research was to investigate the possible application of the magneto-optic apparatus of Allison in the determination of the vitamin content of various substances. The apparatus has been shown to be very sensitive and accurate as well as very rapid in making chemical analyses.

EXPERIMENTAL

The apparatus used for this work consisted of a modified form of the magneto-optic apparatus used by Allison[1] in his work and is shown in Fig. 1. As a source of illumination, a mercury arc was used in connection with a good monochromator adjusted to give the 4358A line only.

A quartz, potassium-hydride, photoelectric cell was used to record the light minima. The current from the photoelectric cell was amplified by the use of a General Electric FP-54 Pliotron tube in a modified DuBridge[2] circuit. The variations in current in the photoelectric cell circuit were recorded by a Leeds and Northrup high sensitivity galvanometer. The photoelectric cell and amplifier circuit including batteries were all placed in a closed metal-covered box to shield them from stray electric fields. The galvanometer which was placed directly on top of this box was also carefully shielded electrically.

Only half of the bilateral trolley system used by Allison was employed in this experiment. The two nicol prisms were held parallel and the magnetic fields in the helices assisted each other; i.e., the fields in the two coils both rotated the plane of polarization in the same direction.

The cylindrical, glass cells used to hold the liquids in this experiment were 16.3 cm long and 2.2 cm in diameter. The ends of the cylinders were flared and then ground. Glass windows were fastened to these flared ends by means of sodium silicate. These cells were placed inside the helices and were held co-axial with them during the experiment.

After the apparatus was set up, it was calibrated and adjusted for its zero position. This was done by using carbon bisulfide in both cells. As a check on the apparatus, minima were also read with different inorganic compounds in one

[1] F. Allison and E. J. Murphy, J. Am. Chem. Soc. **52**, 3796 (1930).

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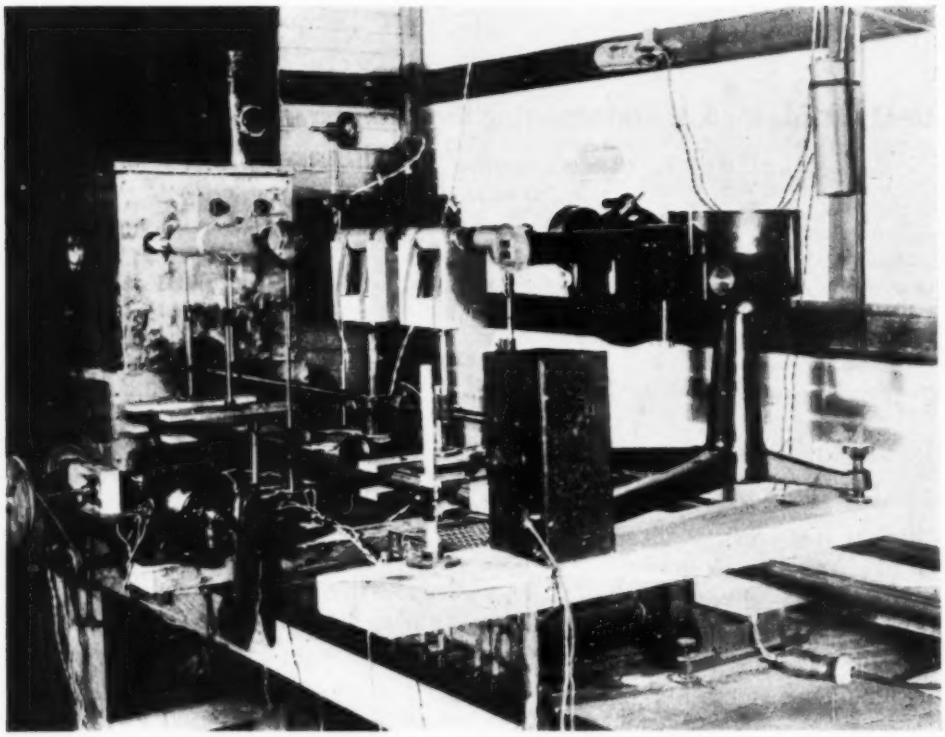

FIG. 1. The plate shows the arrangement of the apparatus. The helices, lenses and nicol prisms are all mounted on a photometer bench. The movable helix was mounted directly on the photometer holder. This helix was moved back and forth along the light path scale by means of a long screw, which is shown on the plate. The large metal covered box, enclosing all of the photoelectric cell and amplifier circuit, is shown at the extreme left. The shielded galvanometer, mounted directly on top of this box, is barely visible because the shield surrounding it was painted a dull black. Part of the control panel for the photoelectric cell and amplifier circuit is shown on the front of the metal covered box. A small reversible, electric motor used to operate the movable trolley may be seen in the lower left-hand corner of the plate. The trolleys and electrical path scale, not shown in this plate, are immediately above this apparatus and are parallel to the photometer bench.

of the cells. Some of the compounds used included hydrochloric acid, nitric acid, zinc chloride, barium chloride, water, ferrous sulphate and ferric chloride. These solutions were all very dilute. The minima found for all these compounds checked very closely with those found by Allison.

In order to find whether there were distinct minima for vitamin A, one of the cells was filled with pure ethyl alcohol and a drop of Haliver oil was added. (The Haliver oil, which had 100 times the vitamin A potency of cod-liver oil, was obtained from Park, Davis and Company of Detroit, Michigan.) Minima were read on this solution as the movable trolley was moved from 0 to 41 along the electrical path scale; i.e., each time the galvanometer showed a deflection, the scale reading was recorded. This procedure was followed five times and the scale readings were then rechecked. Only those scale readings were considered which could be rechecked consistently. Then the tube which contained the Haliver oil in alcohol was thoroughly cleaned and filled with pure alcohol alone. Five sets of minima readings were then taken and rechecked as before. The two final sets of scale readings were then compared and it was found that there were several scale readings which were characteristic of the Haliver oil alone.

Cod-liver oil was next tested in the same manner as Haliver oil and minima were read which were characteristic of this oil. In like manner, other substances containing vitamin A were tested and it was found that all of the substances which were known to be rich in vitamin A content gave

a minimum reading at 32.9 on the electrical path scale. This minimum was therefore concluded to be related to vitamin A.

Since irradiation of cod-liver oil with ultraviolet light reduces the vitamin A potency of the oil, a sample of the cod-liver oil used was irradiated under a quartz mercury vapor lamp for four and one-half hours at a distance of one foot. This sample was tested in the apparatus and it was found that the minimum at 32.9 showed up only very faintly.

A sample of oxidized cod-liver oil was obtained by bubbling air through it for fifteen hours at a temperature of 92±3°C. When this sample was tested, it showed no minimum at 32.9.

Peanut oil and Wesson oil were also tested, but neither of these two showed a minimum at 32.9. Different carotene solutions were also tested. Carotene crystals and a carotene solution, both of which were obtained from Mead Johnson and Co., did not show minima at 32.9. One sample of carotene dissolved in Wesson oil, which had been obtained from the U. S. Department of Agriculture, did show a minimum at 32.9; but this was probably due to slight traces of vitamin A.

Some carotene crystals were dissolved in alcohol and the solution was irradiated under a quartz mercury vapor lamp for a period of four and one-half hours at a distance of one foot. When this irradiated solution was tested, it showed the minimum at 32.9. A similar solution which had not been irradiated did not show this minimum.

Results

A list of the substances tested and the solvent used is shown in Table I. This table also shows whether the minimum at 32.9 appeared for these various substances.

Table I.

Substances	Solvent	Minimum at 32.9
——	alcohol	no
——	water	no
Haliver oil	alcohol	yes
cod-liver oil	alcohol	yes
oxidized cod-liver oil	alcohol	no
irradiated cod-liver oil	alcohol	very faint
irradiated cod-liver oil	water	very faint
spinach juice	alcohol	yes
spinach juice	water	yes
orange juice	alcohol	yes
orange juice	water	yes
tomato juice	alcohol	yes
tomato juice	water	yes
peanut oil	alcohol	no
peanut oil	water	no
Wesson oil	alcohol	no
Wesson oil	water	no
egg yolk	water	yes
carotene (1)	alcohol	no
carotene (1)	water	no
carotene crystals (2)	alcohol	no
irradiated carotene crystals (2)	alcohol	yes
carotene in Wesson oil (3)	alcohol	yes

Carotene (1) solution was obtained from Mead, Johnson and Company, Evansville, Indiana. It had 10 times the antixerophthalmic potency of ordinary cod-liver oil.

Carotene (2) crystals were obtained from Mead, Johnson and Company, Evansville, Indiana.

The carotene (3) in Wesson oil was obtained from the U. S. Department of Agriculture, Bureau of Chemistry and Soils.

The irradiated carotene crystals (2) were irradiated under a quartz mercury lamp for four and one-half hours at a distance of twelve inches.

The egg yolk solution was obtained from the Poultry Husbandry Department of Iowa State College and it was known to contain vitamin A.

The irradiated cod-liver oil was obtained by irradiating Norwegian cod-liver oil under a quartz mercury vapor lamp for four and one-half hours at a distance of twelve inches.

The spinach juice used was obtained from a can of Del Monte spinach.

The orange juice and tomato juice were obtained directly from the fresh ripe fruit.

Discussion

Since the minimum at 32.9 was absent in substances which did not contain vitamin A and present in those substances which did, it was concluded that this minimum is closely related to, or associated with, vitamin A. The fact that the minimum was weakened or destroyed by irradiating or oxidizing the cod-liver oil gave additional strong evidence that it was closely related to the vitamin A content of the oil. Other minima were also examined, but the minimum at 32.9 was the only one for which the evidence was sufficient to indicate a close correlation with vitamin A.

This minimum was not found in any of the carotene solutions except the one carotene-Wesson oil solution. The pure carotene crystals (2) and carotene solution (1) showed no minimum at that point.

Much work has been done in recent years to find the relationship of carotene to vitamin A.

Moore[3, 4] found that carotene behaves *in vivo* as a precursor of vitamin A. von Euler, von Euler, and Hellstrom[5] used the antimony trichloride test on carotenoids and found that they gave a reaction similar to that due to vitamin A, and that carotene from carrots acted the same upon the growth of their test animals as vitamin A.

Bowden and Snow[6] irradiated a solution of carotene in cyclohexane in an atmosphere of nitrogen. Their exciting light was the 2650A line of mercury. After a few hours of irradiation, they found that the solution had a strong absorption band at 3280A, which is characteristic of vitamin A materials. The solution also gave the blue coloration when treated with antimony trichloride in chloroform. From these tests, they concluded that carotene was changed to vitamin A by the action of ultraviolet light. However, their conclusions were questioned by Heilbron and Morton.[7]

In the experiments described here, carotene in an alcohol solution was irradiated with ultraviolet light; and it was found that, after irradiation, this solution gave the minimum at 32.9; whereas, before irradiation, this minimum was not present, indicating that a small amount, at least, of carotene can be transformed into vitamin A by irradiation.

A sample of egg yolk solution was obtained from the Poultry Husbandry Department and tested in the apparatus. This sample was part of the solution used in feeding experiments and it was known to contain vitamin A. This sample also showed the minimum at 32.9 when tested in the apparatus, thus checking the spectroscopic investigations by von Euler and Klussman[8] who found the absorption bands in egg yolk solutions characteristic of vitamin A.

Conclusions

Conclusions which may be drawn from the results of this investigation are as follows:

(1) The magneto-optic apparatus can be used to determine the vitamin content of various substances.
(2) The photoelectric cell may be used successfully with the magneto-optic apparatus.
(3) The minimum at 32.9 on the electrical path scale used shows evidence of being very closely related to the vitamin A content of different substances.
(4) Pure carotene in an alcohol or water solution does not give the minimum at 32.9, but after irradiation with ultraviolet light, it does give this minimum.
(5) The magneto-optic method is very rapid in determining the vitamin content of different substances.

Acknowledgment

The author wishes to express his indebtedness to Dr. J. W. Woodrow, head of the Department of Physics, for furnishing the necessary apparatus and supplies for carrying on this research and for his assistance and guidance throughout this investigation.

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[4] T. Moore, Biochem. J. **24**, 692 (1930).
[5] Beth von Euler, H. von Euler and H. Hellstrom, Biochem. Zeits. **203**, 370 (1928).
[6] F. P. Bowden and C. P. Snow, Nature **129**, 720 (1932).
[7] I. M. Heilbron and R. A. Morton, Nature **129**, 866 (1932).
[8] H. von Euler and E. Klussman, Zeits. f. physiol. Chemie **208**, 50 (1932).

Mutual Impedance of Grounded Wires Lying on the Surface of the Earth when the Conductivity Varies Exponentially with Depth

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This paper presents a formula for the mutual impedance of any insulated wires of negligible diameter lying on the surface of the earth and grounded at their end-points, on the assumption that the conductivity of the earth varies exponentially with depth. Various special cases are briefly discussed.

A FORMULA established by Foster[1] for the mutual impedance of grounded thin wires lying on the surface of a uniformly conducting earth has now been extended to the case of an earth whose conductivity varies exponentially with depth. The formula obtained may also be regarded as a generalization to finite wires on the surface of the earth of a mutual impedance formula recently published[2] for infinite wires at or above the surface of an earth of exponentially varying conductivity. As in that paper, we assume that the conductivity of the earth at depth z is defined by the formula

$$\gamma = \gamma_0 e^{-bz}, \qquad z \leqq 0, \tag{1}$$

where γ_0 is the conductivity at the surface (the x–y plane).

The further assumptions made are, as usual, that the conductivity of the air is zero, that the capacitivities of the earth and of the air are both zero and their inductivities both equal to that of free space ν, where ν has the value 1.256×10^{-6} henries per meter. Finally, all displacement currents have been neglected, so that the frequency $\omega/2\pi$ is restricted to relatively low values.

With these assumptions the differential equations satisfied by the electric field in the earth are

$$\Delta^2 E_x = \Gamma_0^2 e^{-bz} E_x + b(\partial E_z/\partial x), \tag{2}$$

$$\Delta^2 E_y = \Gamma_0^2 e^{-bz} E_y + b(\partial E_z/\partial y), \tag{3}$$

$$\Delta^2 E_z = \Gamma_0^2 e^{-bz} E_z + b(\partial E_z/\partial z), \tag{4}$$

where $\Gamma_0 = (i\omega\nu\gamma_0)^{\frac{1}{2}}$ is the propagation constant at the surface. For positive values of b a solution of Eq. (4) which vanishes at an infinite depth is[3]

$$E_z = \int_0^\infty \int_0^\infty F_z(\mu, \nu) e^{bz/2} K_\alpha(\zeta) \sin \mu x \cos \nu y \, d\mu \, d\nu, \tag{5}$$

where

$$\alpha = [1 + 4\beta^2(\mu^2+\nu^2)]^{\frac{1}{2}}, \qquad \zeta = 2\beta\Gamma_0 e^{-bz/2}, \qquad \beta = 1/b,$$

and F_z is an arbitrary function of its arguments.

Substituting this value for E_z in Eqs. (2) and (3) the following solutions for E_x and E_y are obtained:

$$E_x = \int_0^\infty \int_0^\infty \left\{ F_x(\mu, \nu) K_\alpha(\zeta) + F_z(\mu, \nu) \left[\frac{\mu\Gamma_0}{\mu^2+\nu^2} K_{\alpha+1}(\zeta) - \frac{2\mu\beta e^{bz/2}}{\alpha-1} K_\alpha(\zeta) \right] \right\} \cos \mu x \cos \nu y \, d\mu \, d\nu, \tag{6}$$

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[2] M. C. Gray, Physics **4**, 76–80 (1933).

[3] For the Bessel functions $J_\nu(z)$, $K_\nu(z)$, $I_\nu(z)$ we follow the definitions given by G. N. Watson, *Theory of Bessel Functions*, pp. 40, 78, 77, Cambridge, 1922.

$$E_y=\int_0^\infty\int_0^\infty\left\{F_y(\mu,\nu)K_\eta(\zeta)+F_z(\mu,\nu)\left[\frac{-\nu\Gamma_0}{\mu^2+\nu^2}K_{\alpha+1}(\zeta)+\frac{2\nu\beta e^{bz/2}}{\alpha-1}K_\alpha(\zeta)\right]\right\}\sin\mu x\sin\nu y\,d\mu\,d\nu, \tag{7}$$

where $\eta=2\beta(\mu^2+\nu^2)^{\frac{1}{2}}$, and the functions F_z and F_y are again arbitrary. For negative values of b similar solutions are obtained, with the K functions replaced by the corresponding I functions.

Starting from the solutions (5), (6) and (7), in place of the solutions of the wave equation used by Foster, the impedance formula is obtained by the second method outlined in his paper, and it is found that the mutual impedance of wires S and s lying on the surface of the earth and grounded at their end-points may be expressed in the usual form

$$Z_{12}=\int\int[d^2Q(r)/dS\,ds+\cos\epsilon N(r)]dS\,ds, \tag{8}$$

where the integration extends over the two wires S and s; r is the distance between the elements dS and ds, and ϵ is the angle between their directions. The functions $Q(r)$ and $N(r)$ are defined as follows:

$$Q(r)=(1/2\pi\gamma_0)\int_0^\infty F(\mu)J_0(r\mu)d\mu, \tag{9}$$

$$N(r)=(i\omega\nu/2\pi\Gamma_0)\int_0^\infty f(\mu)J_0(r\mu)\mu\,d\mu, \tag{10}$$

where

$$\begin{aligned}
f(\mu)&=K_{2\beta\mu}(2\beta\Gamma_0)/K_{2\beta\mu+1}(2\beta\Gamma_0), \qquad 0\leqq b,\\
&=I_{-2\beta\mu}(-2\beta\Gamma_0)/I_{-2\beta\mu-1}(-2\beta\Gamma_0), \qquad b\leqq 0,\\
F(\mu)&=(\Gamma_0/\mu)[K_{\alpha+1}(2\beta\Gamma_0)/K_\alpha(2\beta\Gamma_0)-f(\mu)]-2\beta\mu/(\alpha-1), \qquad 0\leqq b,\\
&=(\Gamma_0/\mu)[I_{\alpha+1}(-2\beta\Gamma_0)/I_\alpha(-2\beta\Gamma_0)-f(\mu)]-2\beta\mu/(\alpha-1), \qquad b\leqq 0,\\
\alpha&=(1+4\beta^2\mu^2)^{\frac{1}{2}}.
\end{aligned}$$

In these formulae the distances r, S, s are measured in meters, the impedance Z_{12} in ohms and the conductivity γ in mhos per meter.

The following special cases of the formula may be noted.

(1) If one wire S is straight and infinitely long, the mutual impedance gradient parallel to S and at a positive distance y from S is

$$dZ_{12}/dS=(i\omega\nu/\pi\Gamma_0)\int_0^\infty[K_{2\beta\mu}(2\beta\Gamma_0)/K_{2\beta\mu+1}(2\beta\Gamma_0)]\cos y\mu\,d\mu, \qquad 0\leqq b,$$

$$=(i\omega\nu/\pi\Gamma_0)\int_0^\infty[I_{-2\beta\mu}(-2\beta\Gamma_0)/I_{-2\beta\mu-1}(-2\beta\Gamma_0)]\cos y\mu\,d\mu, \qquad b\leqq 0,$$

a formula which has already been established.[4]

(2) If b is allowed to become negatively infinite while at the same time γ_0 becomes infinite in such a way that $\gamma_1=-\gamma_0/b$ remains finite, Eqs. (9) and (10) become

$$\begin{aligned}
Q(r)&=(1/4\gamma_1)[\mathbf{H}_0(\tfrac{1}{2}i\omega\nu\gamma_1 r)-Y_0(\tfrac{1}{2}i\omega\nu\gamma_1 r)],\\
N(r)&=i\omega\nu/4\pi r-((i\omega\nu)^2\gamma_1/16)[\mathbf{H}_0(\tfrac{1}{2}i\omega\nu\gamma_1 r)-Y_0(\tfrac{1}{2}i\omega\nu\gamma_1 r)],
\end{aligned}$$

[4] Reference 2, page 77.

where $\mathbf{H}_0(z)$ is Struve's function of zero order, and $Y_0(z)$ is the Bessel function of the second kind of zero order as defined by Watson.[5] These values agree with the mutual impedance formula for an earth consisting of a conducting layer at the surface only, as already obtained by Riordan and Sunde.[6]

(3) For small values of b the first terms in the expansions of $Q(r)$ and $N(r)$ in powers of b are

$$Q(r)=1/2\pi\gamma_0 r-(b/4\pi\gamma_0)I_0(\tfrac{1}{2}\Gamma_0 r)K_0(\tfrac{1}{2}\Gamma_0 r)+\cdots,$$

$$N(r)=(1/2\pi\gamma_0 r^3)[1-(1+\Gamma_0 r)e^{-\Gamma_0 r}]+(i\omega\nu b/8\pi)[K_0(\Gamma_0 r)+I_1(\tfrac{1}{2}\Gamma_0 r)K_1(\tfrac{1}{2}\Gamma_0 r)-I_0(\tfrac{1}{2}\Gamma_0 r)K_0(\tfrac{1}{2}\Gamma_0 r)]+\cdots.$$

The terms independent of b in these expansions give precisely Foster's formula for a uniformly conducting earth.[7]

(4) If Γ_0 is small compared with b the first terms in the expansions of $Q(r)$ and $N(r)$ in powers of ω are

$$Q(r)=(1/2\pi\gamma_0)[(1/r)e^{-rb/2}-\tfrac{1}{2}b\,\mathrm{Ei}(\tfrac{1}{2}rb)]+(i\omega\nu br^2/32\pi)\log\omega+0(\omega), \qquad 0<b,$$

$$=(1/2\pi\gamma_0)[(1/r)e^{-rc/2}-\tfrac{1}{2}c\,\mathrm{Ei}(\tfrac{1}{2}rc)-c\log r]+0(\omega), \qquad b\equiv -c<0,$$

$$N(r)=(i\omega\nu/4\pi r)[1-(i\omega\nu r\gamma_0/2b)\log\omega+0(\omega)],$$

where $\mathrm{Ei}(z)$ is the exponential integral as defined by Whittaker and Watson.[8]

In order to obtain convergent integrals in the expansion for $Q(r)$, terms independent of r have been added to the integrand and, after integration, all such terms have been neglected, since they contribute nothing to the mutual impedance. The first term in the expansion gives the direct-current mutual resistance, which has been verified independently.[9]

The term in $\omega\log\omega$, occurring in the expansion of $Q(r)$ for positive values of b, is worthy of mention as it appears to be new. In all previously published cases the expansion in powers of ω has been found in the form

$$Z_{12}=R+i\omega N+o(\omega),$$

where R is the direct-current mutual resistance and N the direct-current mutual inductance of the wires. Reference should be made, however, to the anomalous case mentioned in Riordan and Sunde's paper[10] on the two-layer earth, when the lower layer has an infinite conductivity, a condition which has a formal resemblance to the exponential case when b is large and positive. It is then found that two distinct values of the mutual inductance N are obtained, depending on the order of proceeding to the limits $\omega=0$, $\lambda_2=\infty$. A fuller discussion of this point will be found in the paper cited.

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[5] Reference 3, pages 328, 64.

[6] J. Riordan and E. D. Sunde, Phys. Rev. **37**, 1369–1370 (1931); Bell System Tech. J. **12**, 162–177 (1933).

[7] Reference 1, page 411.

[8] E. T. Whittaker and G. N. Watson, *Modern Analysis*, Third Edition, p. 352, Cambridge, 1920.

[9] This formula for the direct-current mutual resistance for positive values of b was obtained by us in 1930 for use in connection with test measurements of the earth's conductivity, but it was not published at that time.

[10] Reference 6, pages 165–166.

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